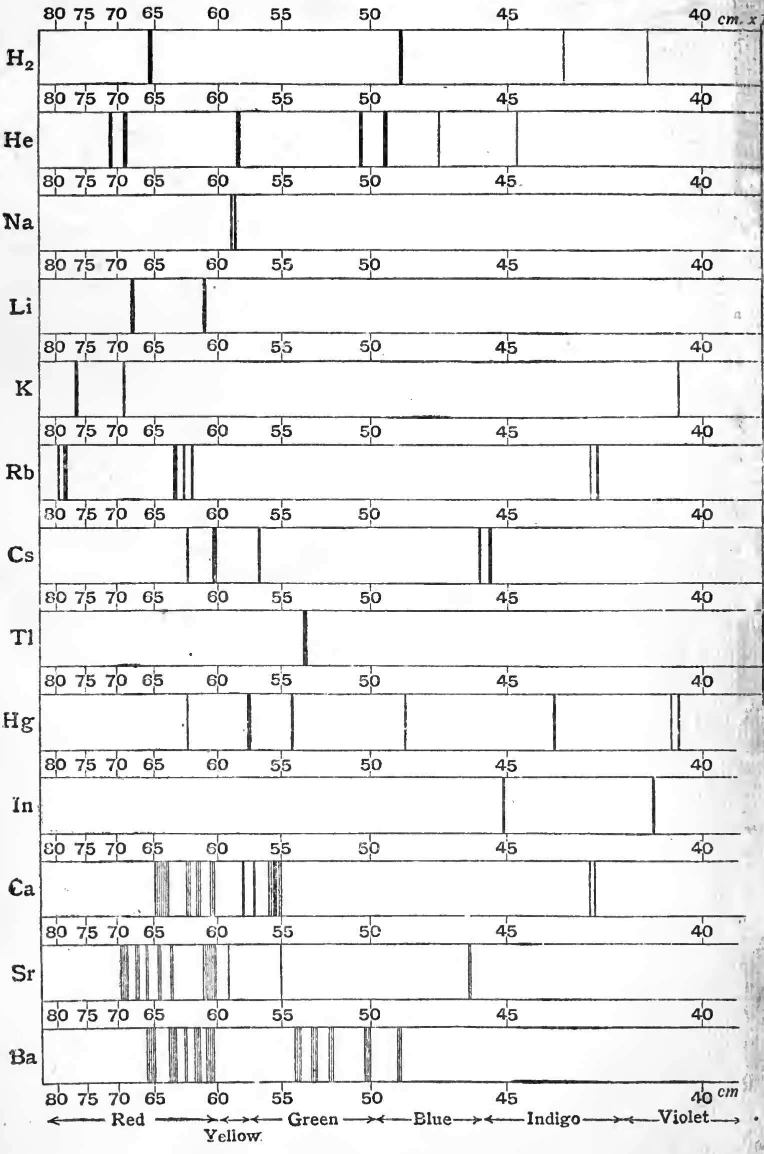

Chart of Spectra, showing positions of Principal Lines.

A TEXT-BOOK OF INORGANIC CHEMISTRY

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A TEXT-BOOK OF INORGANIC CHEMISTRY

FOR UNIVERSITY STUDENTS

BY

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PREFACE

The present text-book, as its title indicates, is primarily intended for students who have completed an introductory course of Matriculation standard, although the more elementary parts of the subject are included so as to make the book complete in itself. It is not written for any particular examination, but should meet the requirements in Inorganic Chemistry of students preparing for the examinations of the Intermediate and Pass B.Sc. of British universities. Brief accounts of technical processes and the elements of Physical Chemistry are included, with worked examples on the latter.

The Atomic Theory and the Periodic Law have been given prominence, since their neglect unfailingly leads to obscurity and triviality. In explaining the foundations of the Molecular Theory I thought it desirable to deviate from the current practice of referring atomic weights to the standard O=16. In my own experience, which is, I believe, that of most teachers, students have sufficient difficulty in reaching a clear understanding of Avogadro's Law without the additional burden of an illogical change of units halfway through the argument. Since there was no obvious necessity to introduce the unit O=16 at a later stage, I refrained from doing so and referred atomic weights to H=1. The table on p. 145 contains all the atomic weights on both standards. *Unless specially stated, all atomic weights given in the book are on the basis* H=1.

Summaries of chapters have been added where they seemed likely to be useful in affording assistance in revision, and examples on all chapters are provided. The student will do well to supplement the numerical questions by additional examples from one of the many text-books on chemical calculations.

Limitations of space prevented more than a bare mention of most of the so-called "Rare Elements," many of which are now of great importance in chemical industry and form part of articles familiar in everyday life. Their chemical properties are also in many cases of unusual interest.

A short account of Werner's theory is given, since the classical theory of Valency, which is of fundamental importance in the somewhat monotonous uniformity of the chemistry of carbon, proves inadequate when any but the very simplest compounds of the remaining elements are under consideration.

The last chapter is intended to be no more than an outline: greater detail in this field would have been inconsistent with the scope of the book, and even undesirable in the present somewhat mobile state of the frontiers of this new knowledge.

It is of the utmost importance that students of Chemistry should have opportunities of examining as many as possible of the substances referred to in text-books and that lectures should be experimental. Practically all the experiments described are shown in the lecture courses at East London College, and the teacher will find no difficulty in supplying the details of manipulation, which through lack of space could not be given in full. Students should realise that descriptions in text-books are necessarily incomplete and need to be supplemented by an acquaintance with the substances themselves. The spurious character of knowledge imparted by mere blackboard methods is painfully familiar to all examiners.

In consulting original sources, reading the proofs, and preparing the index, I have had valuable assistance from my wife. Sir Richard Gregory and Mr. A. T. Simmons have throughout placed their experience freely at my disposal and given me every possible assistance whilst the book was passing through the press. To all who have afforded me help in these and other ways I tender my sincere thanks.

To avoid the multiplication of material the Publishers have allowed me to make use of several illustrations from other books. In this connection the "Treatise on Chemistry" of Roscoe and Schorlemmer; Lowry's "Historical Introduction to Chemistry" (which may be referred to for fuller details on the historical side);

Donington's "Classbook of Chemistry"; Miers's "Mineralogy"; and Tutton's "Crystallography" may be specially mentioned.

The physical properties of substances (densities, boiling points, etc.) have been compiled from the most recent sources, in the hope that the book may also prove useful for reference purposes.

J. R. PARTINGTON.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.
July, 1920.

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CHAPTER I

PURE SUBSTANCES AND MIXTURES

Different kinds of solid bodies.—Different materials may be distinguished from one another by their properties, the most obvious of which is the **physical state : solid, liquid,** or **gaseous.** Many different bodies having the same physical state, however, may easily be distinguished from one another. Thus, coal, sugar, and salt are obviously three different solid bodies ; water and paraffin oil are different liquids, and coal gas and atmospheric air are different gases. These differences we express by saying that the bodies differ in **composition.**

In beginning the study of Chemistry, we meet with a large number of new substances, and the already large number of different bodies known to us in common life appears to be greatly increased.

Thus, if we examine specimens of the following **solids** we find that each has some characteristic **colour,** which enables us to pick it out from the others :

Blue vitriol : blue.
Green vitriol : light green.
Nickel sulphate : bright green.
Cobalt nitrate : purplish-red.
Potassium dichromate : bright red.
Chrome alum : dark purple.
Potash alum : colourless.

All the above solids occur in pieces with definite shapes, called **crystals,** bounded by plane faces meeting in sharp edges. Even if the colour of the solid is not characteristic, we can often distinguish the material by its crystalline form. Thus, the following colourless solids have characteristic shapes :

Alum : octahedra (Fig. 1).
Nitre : long crystals (Fig. 2).
"**Hypo** " : beady crystals (Fig. 3).
Rock salt : cubes (Fig. 4).
Potassium chlorate : scaly crystals (Fig. 5).
Washing soda : lumpy crystals (Fig. 6).

Another distinguishing property is the **density** of the solid. **Lead nitrate,** although it crystallises in the same form as alum, is much heavier.

FIG. 1.—Alum Crystal.

Solids often occur in the forms of powder or lumps, and the crystalline form, although often present in the grains of powder and recognisable under the microscope, may sometimes be absent altogether, even in large pieces. Such solids are said to be **amorphous,** as distinguished from crystalline. The fragments obtained on breaking crystals have sharp edges and plane faces, or show a **crystalline fracture ;** whereas the fractured pieces of an amorphous solid, such as glass or pitch, show curved faces like the inside of a shell, and hence are said to exhibit a **conchoidal fracture.**

Powders of the same colour may often be distinguished by their different densities :

	White.	Red.	Black.
Heavy :	**Barium sulphate**	**Mercuric oxide**	**Manganese dioxide**
Light :	**Magnesium carbonate**	**Ferric oxide**	**Charcoal**

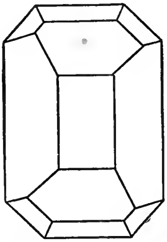

FIG. 2.—Nitre Crystal.

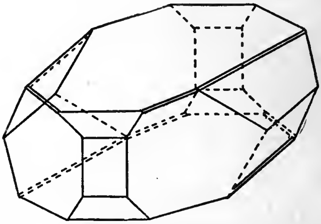

FIG. 3.—Crystal of Sodium Thiosulphate (" Hypo ").

A third method of distinguishing between different solids is by the **solubility** in liquids, such as water. Thus, if finely powdered lead nitrate and barium sulphate, both heavy, white powders, are separately stirred up with hot water in beakers, the former passes into solution, whilst the latter remains undissolved.

Solids when heated usually melt at characteristic temperatures called their **melting points.** Nitre melts at 345°,* potassium chlorate at 350°, " hypo " at 48°, and rock salt at 815°. Barium sulphate melts only at a very high temperature, about 2000°, whilst charçoal has never yet been fused.

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* Temperatures throughout are in degrees Centigrade.

Different kinds of liquids.—The existence of different varieties of **liquids** may be appreciated by examining specimens of the following:

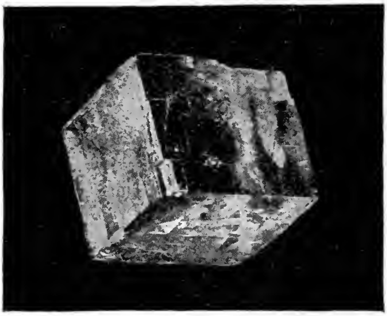

FIG. 4.—Rock-salt Crystal

Water: colourless, odourless, boiling point 100°, density 1.

Alcohol: colourless, spirituous odour, boiling point 78·3°, density 0·79.

Ether: colourless, strong sweet odour, very light and mobile, boiling point 35·6°, density 0·73.

Sulphuric acid: colourless, oily, heavy, boiling point 330°, density 1·85.

Bromine: dark red, suffocating odour, very heavy, boiling point 60°, density 3·1.

Mercury: very heavy, opaque liquid, with metallic lustre, boiling point 357°, density 13·6.

In this table we recognise the **boiling point** as a criterion of the composition of the liquid; this is definite under a fixed pressure, say atmospheric, for a pure liquid. The **freezing point**, or temperature of solidification, of the liquid is another property which may be used for its identification. Water freezes at 0°, bromine at —7·5°, mercury at —39·4°, alcohol at —111·8°, and ether at —113°.

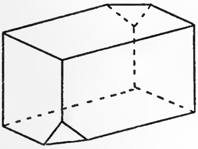

FIG. 5.—Crystal of Potassium Chlorate.

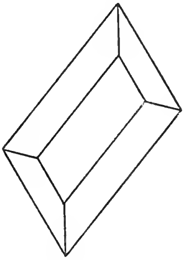

FIG. 6.—Crystal of Washing Soda.

Different kinds of gases.—The existence of different kinds of **gases** was not clearly recognised until the eighteenth century, when Joseph Priestley showed that there were several gases differing from atmospheric air in their properties.

The differences may be appreciated by comparing jars containing the following gases: **oxygen, hydrogen, carbon dioxide, nitric oxide,** and **chlorine.**

By simple **observation** we find that chlorine has a greenish-yellow colour, whilst the other gases are colourless. These colourless gases may, however, be distinguished by appropriate **experiments.**

Expt. 1.—Remove the glass plates from the jars so as to bring the gases in contact with the air. Nothing occurs except with the nitric oxide, which produces deep red fumes.

Expt. 2.—Pour a little lime water into the other jars, and shake. The lime water is unchanged in appearance in all the jars except that containing carbon dioxide, in which it becomes turbid and white.

Expt. 3.—Insert a lighted taper into each of a new set of jars of the gases. In oxygen it burns with a brilliant flame, in chlorine with a smoky red flame, but in the other jars it is extinguished. The hydrogen itself, however, takes fire and burns with a pale blue flame.

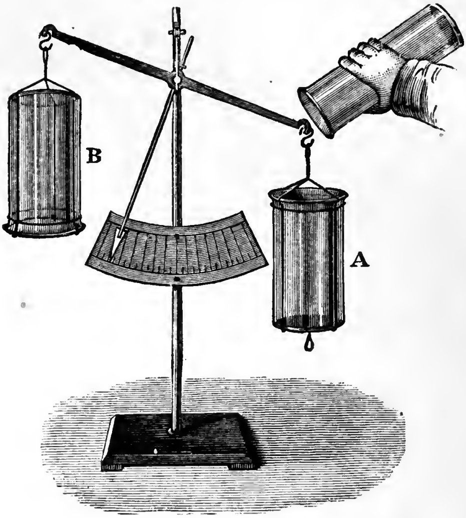

Fig. 7.—Experiment with Carbon Dioxide.

Expt. 4.—If a jar of carbon dioxide is held over a counterpoised beaker on a sensitive balance, and slowly inverted so as to pour the gas into the beaker (Fig. 7), the latter sinks, showing that carbon dioxide is heavier than air, and has passed into the beaker. A taper inserted into the beaker is extinguished.

If a jar of hydrogen is opened, mouth downwards, under an inverted counterpoised beaker (Fig. 8), and slowly inclined so as to pour the gas upwards into the beaker, the latter rises, showing that hydrogen is lighter than air.

Thus, gases differ in density, colour, combustibility, capacity to support combustion, and action on lime water.

Solids and liquids have been distinguished by: colour, form (solids), density, smell, melting point, freezing point, boiling point, and solubility.

Many of these properties may be measured quantitatively, and so the differentiation of the substances rendered more exact. In general, it is sufficient to examine only a few properties in order to identify the material; thus, water and formic acid, although boiling at nearly the same temperature, have different densities, 1·00 and 1·23, respectively, and different freezing points, 0° and 8·3°. Formic acid also has a pungent acid smell.

FIG. 8.—Experiment with Hydrogen.

Pure substances.—Crystals of the same solid, say copper sulphate, usually differ considerably in size, often in shape, yet we should say that all pieces of this material are composed of the same **pure substance**; in other words, so far as composition is concerned, we take no account of accidental circumstances such as size or shape. Again, there are two kinds of phosphorus known in commerce, viz., white and red phosphorus, which differ entirely in appearance and properties. Although these consist of the same material, phosphorus, they are two different substances, since each has specific properties, by means of which it may be recognised.

The group including rock salt, salt from brine springs, purified sea salt, and chemically pure salt made in the laboratory, comprises materials which agree in their properties, apart from size and shape (which we regard in chemistry as non-essential), and we say that all the members of this group are composed of one substance, *common salt.*

Chemistry.—The possibility of arranging materials into groups of definite substances reduces the apparent complexity and scope of their study, because a large number of individual bodies may belong to one group, *i.e.*, be composed of the same substance. The fact that bodies may be arranged in such groups is the fundamental law of Chemistry. **Descriptive Chemistry may be defined as the science which deals with the preparation and properties of substances, and the relations which exist between them.**

In some cases difficulty may arise in defining the properties of bodies, with the view of placing them in groups of substances. Thus, a piece of granite has different properties in different parts. Also, if we base our definition on identity of properties, we shall apparently require an infinite number of groups to accommodate all the possible liquids produced by adding salt to water in varying proportions. These difficulties are removed by a closer study of the cases in which they arise.

Homogeneous and heterogeneous bodies.—Bodies differ according to the properties of their component parts. A body such that all the portions into which it can be divided by mechanical means possess identical properties is called a **homogeneous body.** Thus, glass, water, and air are homogeneous bodies. All pure substances, in the strict sense, are homogeneous bodies, but the converse, as we shall see, is not true.

A body exhibiting different properties in different parts is called a **heterogeneous body.** Thus, a piece of granite is readily perceived by inspection to consist of an aggregate of three different minerals.

One of these minerals is pink, opaque, and capable (though with difficulty) of being scratched with a knife ; it is **felspar.** A second is colourless, transparent, and too hard to scratch with a knife ; this is **quartz.** The remaining mineral is in the form of thin grey, or black, plates, which can be split by a knife into very thin leaves ; it is known as **mica.**

Since the constituents of aggregates such as granite can be separated by mechanical means, heterogeneous bodies are often called **mechanical mixtures.**

The separate parts of a mechanical mixture, or heterogeneous body, are now called **phases.** Quartz, felspar, and mica are three phases existing in granite. A mixture of ice and water consists of two phases, whilst a homogeneous body, even if divided into several parts in space, constitutes only a single phase.

It is not necessary that the parts of a heterogeneous body should be so sharply differentiated as those making up a piece of granite. Quartz crystals often occur which exhibit colouring in different parts (" smoky quartz "), and the intensity of the brown colour, due to impurities, may shade off from one part of the crystal to another. Although we can break off two widely-separated parts of the crystal which appear quite different, and thus satisfy ourselves that the whole crystal is heterogeneous, it is very difficult to fix any position where definite colour change occurs.

Since bodies exist in three states, the following **types of mechanical mixtures** may exist :

(1) **solid + solid** (4) **liquid + liquid** (6) **gas + gas**
(2) **solid + liquid** (5) **liquid + gas** (7) **solid + liquid + gas.**
(3) **solid + gas.**

The ultramicroscope.—The definitions of homogeneous and heterogeneous bodies given above are only relative. Thus, milk, which may seem homogeneous to the eye, is readily seen under the microscope to consist of transparent globules of butter-fat floating in a nearly transparent liquid. In some cases heterogeneity which is not perceptible even by the microscope may be revealed by the scattering of light.

If a few drops of a solution of gum mastic in alcohol are added to water in a glass trough, and stirred, the resulting liquid appears clear, to the eye, even with the aid of the microscope. But if a beam of light from a lantern is passed through the water, before and after the mastic has been added, it will be found that very little light can be seen passing through the clear water, but that the water to which mastic has been added shows the path of the light as a bright, cloudy beam. The same effect is perceived when a ray of sunlight passes through dusty air ; in this case the particles of dust may be seen floating about in the beam.

An instrument making use of this principle is the **ultramicroscope.** This (Fig. 9) consists of an ordinary high-power microscope with the object-glass dipping into the liquid to be examined, contained in a small glass cell. A powerful beam of light, from the sun, or an arc-lamp, is brought, by means of a lens, to a focus in the liquid lying just under the microscope. The presence of suspended particles in the liquid is then revealed by the light scattered from them, and they appear as bright specks.

Whilst microscopic visibility ceases with particles of diameter about $1{\cdot}5 \times 10^{-5}$ cm., or $0{\cdot}15\mu$ ($\mu = 0{\cdot}001$ mm.), the ultramicroscope reveals particles down to 5×10^{-7} cm., or $5\mu\mu$ ($\mu\mu = 10^{-6}$ mm.), or about one-hundredth the wave-length of visible light, which is 4×10^{-5} cm. in the case of violet light, and 8×10^{-5} cm. in the case of red light.

By the action of phosphorus on a solution of gold chloride, ruby-red, apparently clear, solutions are obtained. These, under the ultramicroscope, exhibit particles, which have been shown to be about $5\mu\mu$ in diameter. Suspensions of this kind, containing ultramicroscopic particles, are called **colloidal solutions.** Still smaller particles of gold, not visible even with the ultramicroscope, can act as nuclei, or centres of condensation, for the production of ultramicroscopic particles, and the diameter of these nuclei has been estimated at 10^{-7} cm. Zsigmondy, the inventor of the ultramicroscope, therefore distinguishes three kinds of small particles in liquids: **microns,** microscopically visible, diameter 10^{-3} to 10^{-5} cm. (ordinary suspensions); **submicrons,** ultramicroscopically visible, diameter 10^{-5} to 5×10^{-7} cm. (colloidal solutions); **amicrons,** invisible, but act as nuclei, diameter 10^{-7} cm. (colloidal solutions).

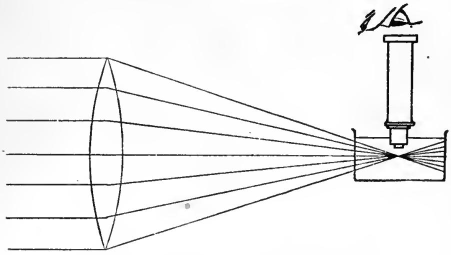

FIG. 9.—Diagram of Ultramicroscope.

If a few drops of a solution of the red dye eosin be added to a trough of water, through which a beam of light is passed, the path of the beam is rendered visible by a beautiful green light, which is not unlike the haze obtained with the mastic, except that it is coloured. Under the ultramicroscope, however, no particles can be detected, and the phenomenon is quite different from that shown by turbid liquids; the effect is known as **fluorescence.** The two effects are readily distinguished by the fact that the light from turbid media is polarised, whilst fluorescent light is not.

Matter may also be produced in the form of very thin films, of the same order of thickness as the ultramicroscopic particles. Thus, gold-leaf is beaten out to a thickness of only 10^{-5} cm., and if a piece of burning magnesium ribbon is held behind a piece of gold-leaf pressed between two sheets of glass, the gold is seen to be translucent, and to let through a green light.

Atoms.—We shall see later that there is a good deal of direct evidence that *all* kinds of matter are made of exceedingly small particles called **atoms,** which have diameters of the order of 10^{-8} cm. These cannot be seen even by the ultramicroscope, but are brought into evidence in other ways when X-rays are used instead of ordinary light. These X-rays differ from light only in having a much smaller wave-length, of the order of 10^{-8} cm., and if they are allowed to fall on a crystal, such as rock salt, the effect produced is similar to the colour phenomena seen with visible light falling on thin films such as soap-bubbles. The X-rays are not visible, but the effect can be detected, and it indicates that the crystals are made up of layers of atoms, separated by distances of the order of 10^{-8} cm.(Chap. LI).

Thus, in reality, all kinds of matter are heterogeneous, since they are aggregates of atoms. In practice, we limit the use of the word heterogeneous to bodies seen by the ultramicroscope to consist of different parts, and speak of other bodies as homogeneous.

The separation of the constituents of mixtures of solids.—The separation of the phases of a mixture of solids may be effected in many different ways.

(1) **Mechanically,** by picking out the different bodies, if the system is sufficiently coarse-grained.

(2) By differences of **density,** say by stirring up a powder with an inert liquid, the density of which lies between that of one of the solids and those of the others. Thus, in powdered granite, the minerals have the following densities: felspar, 2·57; quartz, 2·65; mica, 2·85. Hence, if the powder is shaken with a mixture of density 2·6, composed of the liquids benzene, density 0·874, and methylene iodide, density 3·33, the felspar will float, whilst the mica and quartz will sink. The two heavier minerals may then be separated by another mixture of the liquids of density 2·7.

(3) By **magnetism**; iron filings may be separated from admixture with flowers of sulphur by their attraction to a magnet, leaving the sulphur behind.

(4) By **electrification**; if a mixture of red lead and flowers of sulphur is dusted on an ebonite plate rubbed with flannel, the red lead, which becomes charged positively, adheres to the plate, which is charged negatively, whilst the sulphur, which has the same charge as the plate, does not adhere. If the plate is now tapped gently on a sheet of paper, the sulphur with only a little red lead falls off, leaving the red lead on the plate; this may be brushed off on to the paper, and the colours of the two powders compared.

(5) By the different attractions of the solids for a liquid (**surface**

tension); thus, if a mixture of powdered zinc blende (native zinc sulphide) and sand is sprinkled on the surface of water, the sand is wetted and sinks, but the blende is not wetted, and floats, although it is heavier than water.

(6) By the different **solubilities** in a liquid; if the mixture of iron filings and sulphur is shaken with carbon disulphide the sulphur dissolves, and the solution may be decanted from the iron, which is insoluble. If the solution of sulphur is poured into a dish, covered with a filter paper, and the solvent allowed to evaporate, fine crystals of sulphur are left (Fig. 10).

(7) By **fusibility**; if a mixture of lead shot and sand is heated in a crucible, the lead fuses, and the sand floats to the top.

(8) By **volatility**; if a mixture of sand and sulphur is heated in a test-tube, the sulphur boils, giving a reddish-brown vapour which condenses on the cool sides of the tube as a yellow **sublimate,** whilst the sand is left in the bottom of the tube. A mixture of sand and iodine behaves similarly, the iodine forming a beautiful violet vapour, which condenses on the cool tube as a black crystalline sublimate.

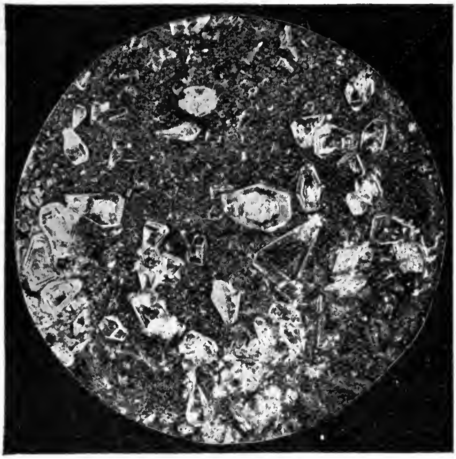

FIG. 10.—Sulphur Crystals.

The magnetic method is used to separate minerals such as *tinstone* (density 6·4–7·1) and *wolfram* (density 7·1–7·9), which occur together, and are so nearly alike in density that they cannot be separated by washing with a stream of water. Tinstone is non-magnetic, whilst wolfram (an ore of tungsten, a metal used in making the filaments of electric lamps) is fairly magnetic. The crushed ore is dropped on a travelling belt (Fig. 11), and falls off near a powerful electromagnet. The tinstone falls undeflected, but the wolfram is pulled towards the magnet, and forms a separate heap. The process is called **electro-magnetic separation.**

Separation by surface tension is used in the **flotation process** for separating minerals, such as zinc blende, which is not easily wetted by water, from galena (an ore of lead), which is. The crushed ore is agitated, by a blast of air, with water, to which a little oil, *e.g.*, of eucalyptus, has been added. The blende forms a scum on the surface, whilst the galena sinks.

The separation of solids from liquids.—Solids mixed with liquids may be separated in various ways.

(1) By settling out under the influence of gravity, *i.e.*, by **sedimentation.** The coarser the particles, the more rapidly they settle.

The **rate of settling** of spherical particles, solid or liquid, in a liquid or gas is given by **Stokes's equation** :

$$c = \frac{2}{9}\frac{r^2 g}{\eta}(d - d') \text{ cm. per sec.};$$

where r = radius of the particles in cm. ; g = acceleration of gravity, 981 cm. per sec. per sec. ; η = viscosity of the liquid in C.G.S. units ;

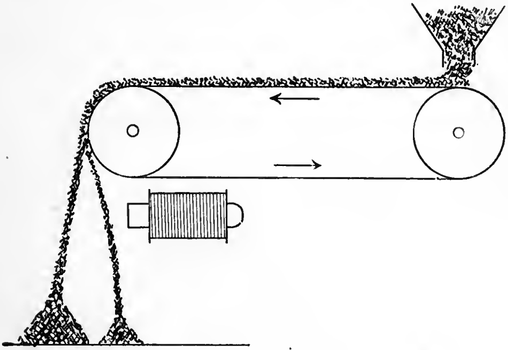

FIG. 11.—Diagram of Electromagnetic Separation.

d and d', the densities of the suspended particles, and of the liquid, respectively. (If $d < d'$, the particles *rise* ; *e.g.*, air bubbles in water.)

The **viscosity** of a liquid is a measure of the resistance encountered in stirring it; ether is a liquid of small viscosity, treacle one of great viscosity.

If we calculate from Stokes's formula the rates of deposition of particles of sulphur ($d = 2{\cdot}06$) in water ($d = 1{\cdot}00$; $\eta = 11{\cdot}4 \times 10^{-3}$ at 15°), the diameters of the sulphur particles being 0·1 cm., and 0·0001 cm., we find these rates to be 203 cm. per sec., and 0·000203 cm. per sec., respectively. The fine particles remain almost permanently in suspension, forming a colloidal solution (see p. 8).

Particles of different sizes mixed together may be separated by **fractional sedimentation** ; the powder is stirred up with water, and the time of settling divided into a number of intervals. A series of powders increasing in fineness is thus obtained. The process may be repeated with each of these. This method is used in separating fine clay from coarse earth, for the manufacture of porcelain.

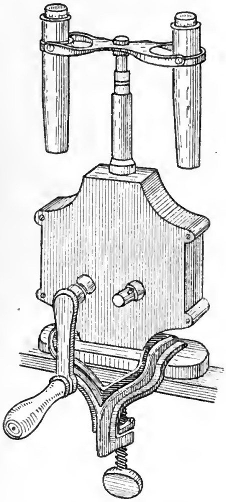
FIG. 12.
Centrifugal Machine.

(2) By **centrifugal force.**—A centrifugal machine is shown in Fig. 12. Two aluminium tubes are attached by hinges to a central shaft, which may be rotated at high speed (2000 revs. per min.) by means of gearing and the handle. If a glass tube is filled with the fine suspension of barium sulphate obtained by adding dilute sulphuric acid to a solution of barium chloride, and is placed in one of the aluminium tubes, a similar tube of water being put in the opposite side as a counterpoise, the powder is separated on the bottom of the tube on working the machine. A comparison tube of the suspension, kept at rest, does not settle during the time of the experiment.

(3) In many cases suspended particles are charged electrically, and move in an electric field; this motion is known as **cataphoresis.**

EXPT. 5.—A **colloidal solution** of arsenic sulphide (*i.e.*, a suspension of very fine particles) is made by pouring a solution of arsenic trioxide in boiling water into a solution of sulphuretted hydrogen in water, and driving out the excess of the latter gas by a stream of hydrogen. About 50 c.c. are taken, and about 5 gm. of urea dissolved in it to make it denser than water. The yellow solution is carefully run by a pipette into the lower part of a **U**–tube half filled with distilled water. Platinum plates fitted through glass tubes by platinum wires are placed in each arm of the tube, and connected with the supply mains (220 volts). The level of the arsenic sulphide, as marked by paper rings, soon falls on one side of the **U**–tube, and rises on the other (Fig. 13). The fact that the colloidal solution contains suspended particles may be seen by passing a beam of light through some of it in a beaker.

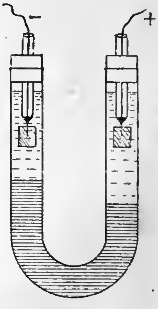

FIG. 13.
Cataphoresis.

If a few drops of sulphuric acid are added to the colloidal solution of arsenic sulphide, an immediate precipitation in yellow flocks occurs. If the mixture is now shaken with paraffin oil, the latter rises to the surface, carrying the yellow arsenic sulphide with it. This is an application of the **flotation process** (p. 10) : arsenic sulphide adheres more strongly to oil than to water.

(4) The commonest method of separating solids from liquids is by **filtration.** The liquid containing the suspended **precipitate** is poured on a filter, consisting of a folded cone of unglazed paper in a glass funnel. The liquid passes through the pores of the paper under the action of gravity, but the solid particles, if larger than the pores of the paper, are kept back.

Particles which are very small pass through the filter. Thus, the precipitate of barium sulphate prepared above runs as a milky liquid through an ordinary filter paper. A special " barium sulphate paper," of fine texture, may then be used. The size of the particles of this precipitate may be increased by precipitating a boiling solution of barium chloride with boiling dilute sulphuric acid. The barium sulphate then settles out very rapidly, and is easily filtered.

Hot solutions filter more rapidly than cold ones, since the viscosity of the liquid is reduced by raising the temperature, and the process of filtration is really the passage of liquid through capillary tubes, the speed increasing as the viscosity diminishes.

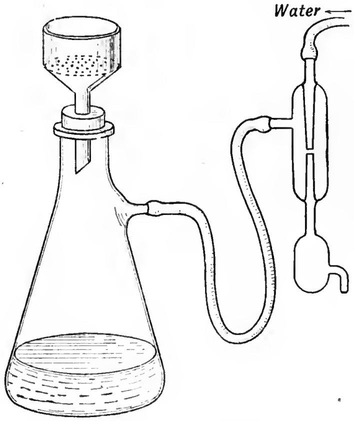

FIG. 14.—Apparatus for Filtration under Reduced Pressure.

The rate of filtration is also increased by increasing the difference of pressure between the two ends of the capillary pores of the filter. This is effected by **filtration under reduced pressure.** The filter paper is laid flat on the perforated grid of a porcelain **filter funnel** (Büchner funnel) (Fig. 14), which is fitted air-tight through a rubber stopper into a tubulated **filter flask.** The side tube of the filter flask is connected with a **filter pump,** actuated by a stream of water from the mains. The air is removed from the flask, and the pressure *difference* on the two sides of the paper thus increased. Such filter funnels should not be allowed to become empty during filtration and washing, as then air-channels are formed in the precipitate. In washing precipitates in ordinary funnels, on the contrary, each lot of liquid should be allowed to drain out before the next is added.

The separation of liquids from liquids.—If chloroform and water are shaken together in a **separating funnel** (Fig. 15), and then allowed to stand, the heavy chloroform settles out in a layer at the bottom, and can be run off through the tap, leaving the water in the bulb of the funnel.

A suspension of *fine* droplets of one liquid in another is called an **emulsion.** Thus, milk is an emulsion of droplets of fat in a watery liquid. Each liquid alone may be transparent, but the emulsion is turbid, owing to the scattering of light from the small particles.

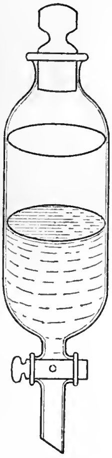

FIG. 15. Separating Funnel.

Emulsions can often be separated by centrifugal force; milk is separated partially in this way into cream (rich in fat), and separated milk (poor in fat).

If one liquid is soluble in a third, whilst the second is not, a separation may be effected by shaking with the third liquid. If ether is added to an emulsion of paraffin oil and water in a separating funnel, and shaken with it, the ether dissolves the paraffin, and the solution floats to the surface. The water may be run off below, and the ethereal solution allowed to evaporate on a water-bath (Fig. 16), leaving the oil.

The separation of gases from liquids and solids.—Gases mix with each other in all proportions, so that heterogeneous systems can be obtained with gases only transiently, when a light gas is stratified on a heavier one. The line of demarcation is not sharp, and the gases soon mix by **diffusion.**

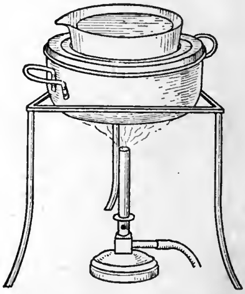

FIG. 16.—Evaporation on a Water-bath.

EXPT. 6.—Pass carbon dioxide into a large jar, so that the latter is partially filled with the gas (Fig. 17). Blow a bubble with Plateau's soap solution * and allow it to fall into the jar. It is arrested on reaching the carbon dioxide, and remains suspended. If a taper is lowered into the jar, it is extinguished on reaching the level of the bubble.

A suspension of minute bubbles of gas in a liquid forms a **froth**

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* **Plateau's Soap Solution** is prepared as follows. 10 gm. of sodium oleate and 400 c.c. of distilled water are allowed to stand at the ordinary temperature in a stoppered bottle until solution occurs. 100 c.c. of pure glycerin are then added, and the liquid, after shaking, is allowed to settle for a few days in the dark. The clear liquid is decanted or siphoned off, and, after the addition of 1 drop of ammonia, is preserved in a stoppered bottle covered outside with opaque black varnish.

or **foam.** It is usually produced by shaking the gas with a liquid of low surface-tension, such as soap solution. Froths may be separated by centrifugal force, or by adding other liquids, such as alcohol to aqueous foams.

A suspension of minute droplets of liquid in a gas, such as is produced by rapidly cooling moist air, is called a **mist** or **fog.** In fogs the particles are smaller, and a mist may pass over into **rain** when the particles of liquid unite by coalescing into large drops.

Aitken showed that mists are produced by condensation on minute solid particles of dust (**motes**) floating in the air; if these are partially removed, say by filtering the air through cotton-wool, then, on cooling, condensation occurs on the few remaining nuclei, producing rain-like drops. If the nuclei are all removed, by allowing the air to stand for some time in a vessel with wetted sides, then condensation does not occur at all until the air has been cooled much below the temperature at which mist-formation previously took place.

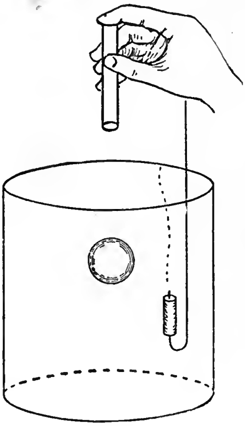


FIG. 17.—Experiment illustrating Stratification of Gases.

C. T. R. Wilson found that minute electrically charged nuclei, called **gaseous ions,** which are produced even in dust-free air by electric sparks, or exposure to X-rays, can also act as condensation centres. They may also be filtered out by cotton-wool (Chap. LI).

A suspension of fine particles of solid in a gas is called a **smoke** or **fume.** Coal smoke consists of small particles of carbon, which when they aggregate together form soot. The smoke from the glowing tip of a cigarette, which also consists of small particles of carbon, appears blue, because the particles are very fine, their diameters being of the order of a wave-length of light. Smoke rising vertically from a chimney in clear dry air also appears blue. The smoke some distance from the end of the cigarette, or blown from the mouth, and smoke from a chimney on a damp day, appear greyish-white and opaque, because the particles are larger, probably as a result of the condensation of moisture upon them.

The particles of fogs and smokes are often electrically charged, or become so on exposure to a high-tension discharge such as is given off from a point or fine wire attached to a pole of an electrical machine or induction coil. During such discharges, the fume is often precipitated, as was shown by Sir Oliver Lodge in 1883. This method of fume dissipation has recently been applied by

Dr. F. G. Cottrell, in America, to the precipitation of fumes from smelting furnaces, blast-furnaces, cement-furnaces, etc.

Expt. 7.—Fill a bell-jar with fumes of ammonium chloride by passing air through two flasks containing strong hydrochloric acid and ammonia solution, respectively (Fig. 18). Place the bell-jar on a metal plate connected with one pole of an induction coil, or Wimshurst machine, and connect the other pole with a pointed copper wire passing through a rubber stopper in the bell-jar. On electrifying the apparatus, the fume rapidly settles. A comparison plain jar filled with fume is placed beside the first one, to show the persistence of the fume without treatment.

The **Cottrell apparatus** consists of tubes or chambers containing electrodes, between which a high tension of 75,000 volts is maintained. The solid deposited from the fume passing through is shaken off the sides of the tube or chamber from time to time by tapping with an automatic hammer; liquids flow away without such treatment.

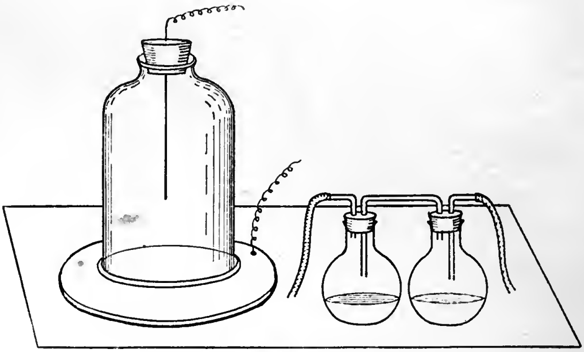


Fig. 18.—Electrical Fume Precipitation.

SUMMARY OF CHAPTER I

Different kinds of matter exist, characterised by different properties when examined under the same conditions. Some masses of matter are **homogeneous,** *i.e.*, of the same kind throughout, whilst others are **heterogeneous,** *i.e.*, of different kinds in different parts of the mass. All the parts of a heterogeneous mass may be separated from one another by suitable means, depending on differences in density, magnetic and electrical properties, surface-tension, solubility, volatility, fusibility, etc.

EXERCISES ON CHAPTER I

1. Describe some of the means available for differentiating between various kinds of solid bodies. If you were given two white powders, one of which was silica and the other lead carbonate, how would you determine which was which by non-chemical means ?

2. Tabulate the various methods used in the separation of mechanical mixtures of : (*a*) solids and liquids, (*b*) solids and solids, (*c*) liquids and liquids, (*d*) gases and liquids, pointing out methods common to the four classes. In which classes of heterogeneous bodies would you place (*a*) milk, (*b*) snow, (*c*) pumice-stone, (*d*) white paint ?

3. Explain what is meant by the terms : phase, heterogeneous, homogeneous, colloidal solution, precipitate. Discuss the use of the term *heterogeneous* as applied to matter in general.

4. Compare the rates at which particles of silica (density 2·65) of diameters 0·25 and 0·01 mm., respectively, settle in water. How may the rate of settling be accelerated ?

5. How are (*a*) flotation, (*b*) electric precipitation, (*c*) electromagnetic separation, applied on the large scale ?

CHAPTER II

ELEMENTS, COMPOUNDS, AND SOLUTIONS

Chemical changes.—It is a matter of common observation that bodies often undergo radical changes under certain conditions. Thus, wine on standing exposed to air may lose its colour, and become sour; bright copper becomes dull, and ultimately covered with a green crust, when exposed to moist air, and under the same conditions iron rusts away completely to a brown powder. A candle burns away, and apparently disappears.

In other cases the changes appear to be much less deep-seated, and the properties of the materials are only slightly, and temporarily, modified. Thus, water on cooling freezes to ice, but the ice melts, and is reconverted into water, on warming. A bar of iron which has been heated to redness is only slightly altered and, apart from a little scale on the surface, is recovered without change on cooling.

Expt. 8.—Heat in a Bunsen flame a piece of platinum wire. The wire becomes red-hot, but on cooling is apparently quite unchanged. Repeat the experiment with a piece of magnesium ribbon. The ribbon takes fire and burns with a brilliant white flame, producing a white ash.

Material changes are found, by such observations and experiments, to be divisible into two large but not sharply defined classes: either they affect only a few properties of the material, and are temporary, or they are much more drastic, resulting in the disappearance of the original material as such, and the formation in its place of a different material. Changes of the first class are called **physical changes**; those of the second class, **chemical changes.**

Expt. 9.—Place a small piece of yellow phosphorus on a sand-tray, and sprinkle over it a few crystals of iodine. The phosphorus takes fire.

Expt. 10.—Pour into separate test-glasses a little of the following solutions: potassium ferricyanide, tannin, potassium thiocyanate, caustic potash. Add to each glass a dilute solution of ferric chloride. A blue, black, blood-red, and brown liquid, respectively, is produced.

Expt. 11.—Heat a small pill of mercuric thiocyanate by the flame of a taper. The substance swells up into a worm-like mass of a friable brown substance (" Pharaoh's Serpent ").

Expt. 12.—Heat a mixture of 5 parts of fine iron filings and 3 parts by weight of flowers of sulphur in a test-tube. The sulphur boils, and then the iron begins to glow, and continues to do so when the tube is removed from the flame. When the glowing ceases, heat the tube for a short time, then allow it to cool by placing it on a tray of sand. When cold, break the tube carefully in a mortar. A greyish mass is obtained, which is easily powdered in the mortar. The powder is black, and under a lens no iron or sulphur particles can be distinguished in it. It yields no sulphur when treated with carbon disulphide (p. 10), and if a magnet is brought over it, the powder is completely attracted (although it must be removed in portions since it is not so magnetic as iron), leaving no residue of sulphur, as was the case with the original mixture. The iron and sulphur have formed a new substance, called **iron sulphide.**

From these experiments it is seen that chemical changes are often accompanied by an **evolution of heat.** This, however, is by no means always the case, since sometimes heat is absorbed.

Expt. 13.—Pour concentrated hydrochloric acid over crystals of Glauber's salt in a beaker. The crystals fall to a granular white powder, which may be recognised, if filtered off, as common salt. A considerable **absorption of heat** occurs, and the beaker feels very cold. If a small test-tube of water is placed in the mixture in the beaker, the water is quickly frozen.

The law of conservation of matter.—The quantity of matter in a body is measured by its **weight.** The weight of a body, however, depends on the force of gravity attracting the body to the centre of the earth, and the latter varies slightly from place to place on the surface of the earth. In the ordinary balance this slight variation affects equally both the body weighed and the weights used in the other pan, so that the weight appears always to be the same. If a spring-balance is used, slight differences are found in different localities, since the weight is then measured directly by the extension produced in a spring by the attraction of gravity. The name **mass** is therefore used to indicate the property of the body of resisting the action of forces tending to set it in motion, one such force being gravity. The mass of a body is supposed to be an unalterable property of the body itself, and a measure of the **quantity of matter** contained in the body.

The ancient philosophers had views on the ultimate fixity of the material world. Thus, Empedocles (B.C. 490–430), as quoted by Aristotle, says: "Nothing can be made out of nothing, and it is impossible to annihilate anything. All that happens in the world depends on a change of form and upon the mixture, or separation, of bodies." This is strikingly similar to the statement of the French chemist Lavoisier (A.D. 1743–1794), made about 2300 years later: "Nothing can be created, and in every process there is just as much substance (quantity of matter) present before and after the process has taken place. There is only a change or modification of the matter." Lavoisier's statement, however, differed from that of Empedocles: whereas the statement of the Greek philosopher was merely an unverified opinion, that of Lavoisier was a scientific truth, founded upon experiment.

The early chemists, with one or two exceptions, entirely ignored the changes of weight occurring in chemical processes. Usually they considered such matters as removed from purely chemical studies, and beneath their notice. Thus, Jean Rey (1630) says: "The examination of weights by the balance differs from that made by the reason. The latter is only employed by the Judicious, whilst the former can be practised by the Veriest Clown. The latter is always exact, whilst the former is seldom without deception."

Joseph Black (1755), in a research on magnesia, paid careful attention to the weights of the materials. "Three ounces of magnesia were distilled in a glass retort and receiver. When all was cool, I found only five drachms of whitish water in the receiver . . . the magnesia when taken out of the retort . . . had lost half its weight . . . It is evident that of the volatile parts contained in the powder, a small portion only is water; the rest cannot, it seems, be retained in vessels under a visible form . . . and is mostly *air* [carbon dioxide]." Thus, when Black found a loss of weight in a chemical change, he put it down to the escape of some material which had escaped attention, and he began to look for this material. In doing this, he recognised implicitly the principle stated later by Lavoisier. Black's experiment is an example of many chemical changes in which an apparent destruction of matter is due to the escape of a **gas**, which is very likely to be overlooked unless special search is made for it. Since the existence of gases was not recognised clearly until the eighteenth century, it is not surprising that a belief in the actual destruction of matter should have survived until that period.

Experiments on the conservation of matter.—When a candle burns, it is apparently completely destroyed. It is easy to show by experiment that this is not the case.

Expt. 14.—Fit a small candle through a cork, in which there are four holes bored to admit air, into a glass tube 2 in. wide and 8 in. long, in which a piece of wire-gauze is supported by three wires from the top. Sticks of caustic soda, supported on a few pieces of quicklime, are placed on the top of the gauze, and the whole apparatus is counterpoised on one arm of a balance (Fig. 19). Light the candle, and allow it to burn. In a few minutes the arm of the balance carrying the apparatus is depressed, showing that, so far from a loss of weight occurring when a candle burns, there is an increase of weight if the products of combustion are prevented from escaping by absorption in caustic soda. The nature of these products may be found by the following experiments.

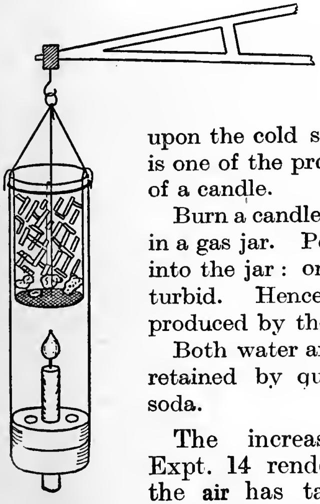


Fig. 19. Burning of a Candle.

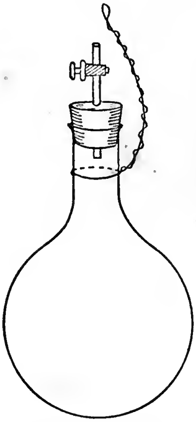


Fig. 20.—Flask for Weighing Air.

Expt. 15.—Hold a dry bell-jar over a burning candle. The sides of the jar are at once dimmed by moisture deposited upon the cold surface. Hence **water** is one of the products of combustion of a candle.

Burn a candle, supported by a wire, in a gas jar. Pour a little lime-water into the jar: on shaking, it becomes turbid. Hence **carbon dioxide** is produced by the combustion.

Both water and carbon dioxide are retained by quicklime and caustic soda.

The increase in weight in Expt. 14 renders it probable that the **air** has taken some part in the combustion, and that the products of combustion, which are absorbed by the caustic soda, contain part of the air. If this is the case, air must possess weight. Although the ancients believed that air was without weight, the opposite was proved by the following experiment of Otto von Guericke, the inventor of the air-pump (1650).

Expt. 16.—Evacuate by an air-pump, and counterpoise on the balance a 2-litre globe, fitted with a stopcock through a rubber cork (Fig. 20). Open the stopcock, and notice the hissing noise of the air rushing into the globe. Replace the globe on the balance, and notice that the side of the beam on which it hangs is now depressed.

In order to test the truth of Lavoisier's statement, it is obvious that the chemical change, or **chemical reaction,** as it is usually called, must be instituted in a closed space, so that none of the materials used can escape.

EXPT. 17.—Place a *small* piece of phosphorus, dried by pressing between filter paper, in a dry strong round-bottom flask of about 250 c.c. capacity, fitted with a good rubber stopper. Weigh the flask. Warm over a flame the spot where the phosphorus lies until it ignites. When the combustion is finished, allow the flask to cool, and reweigh. The weight is unchanged.

EXPT. 18.—Pour a little mercuric chloride solution into a conical flask, and place inside a small tube containing a solution of potassium iodide. Cork the flask (Fig. 21), and counterpoise on the balance. Now tilt the flask so that the solutions mix. A red precipitate of mercury iodide is formed, but the weight will be found to be unchanged.

FIG. 21.—Experiment on the Law of Conservation of Matter.

The generalisation stated by Lavoisier is called the **Law of Conservation of Matter,** or the **Law of Indestructibility of Matter.** It is true both for physical and for chemical changes. Some very exact experiments have been made to test the degree of accuracy of the law.

Stas (1865) took 27·6223 gm. of pure silver, and 32·4665 gm. of pure iodine, and by a roundabout series of chemical reactions converted them into silver iodide, which weighed 60·0860 gm. The loss of weight is only 0·0028 gm., or 0·00005 of the total weight. E. W. Morley (1895) combined 30·3429 gm. of pure oxygen with 3·8211 gm. of pure hydrogen, and obtained 34·1559 gm. of water. The loss of weight is 0·0081 gm., or 0·0002 of the total weight.

Landolt's experiments.—Until 1900 the law of conservation of matter was regarded as accurate within the limits of experimental error, which were very small. In that year, however, Heydweiller stated that he had observed small losses of weight when certain chemical reactions were carried out in sealed vessels. Thus, when 80 gm. of copper sulphate, dissolved in 130 c.c. of water, were decomposed with 15 gm. of metallic iron, there was a loss of weight of 0·217 mgm. H. Landolt in 1893 began a series of experiments, which were not completed until 1908, with the object of testing the law of conservation of matter with all possible accuracy, and of determining whether the deviations noticed were real, or due to some error of experiment.

In the separate legs of a Jena glass **U**-tube (Fig. 22) Landolt sealed up solutions of substances capable of reacting without the production of much heat, so that the disturbances arising from this cause could be eliminated. He used :

1. Silver sulphate and ferrous sulphate, giving a precipitate of metallic silver.
2. Hydriodic acid and iodic acid, giving a precipitate of iodine.
3. Iodine and sodium sulphite, giving sodium iodide and sulphate.
4. Chloral hydrate and caustic potash, giving an emulsion of chloroform.

The tube was counterpoised against an exactly similar tube on a balance capable (in the final experiments) of detecting a change of weight of 0·0001 gm. with a load of 1 kgm. in each pan, *i.e.*, a change of 1 part in 10,000,000. One reaction tube was then inverted, after removing it from the balance, and the chemical change allowed to take place. After cooling, the tube was replaced on the balance, and the change in weight, usually a diminution, noted. The other tube was then taken off and inverted, and the process repeated. At first, slight diminutions in weight, amounting to 0·167 mgm. in the maximum, were always found, but after a long series of experiments these were traced to two causes : (*a*) as a result of the slight evolution of heat, the film of moisture condensed on the outer surface of the glass was partially driven off, and did not return until after long standing ; (*b*) the vessel expanded slightly as a result of the slight increase of temperature, and did not return to its original volume until some time had elapsed. In consequence of the first error, the weight of the vessel was reduced, and the second error, which led to an increase in the volume of air displaced by the vessel, also reduced the apparent weight. By allowing the vessel to stand for a long time after the experiment, before reweighing, Landolt found that it recovered its original weight to within 1 part in 10,000,000—*i.e.*, within the limits of experimental error. For these reactions, therefore, the law of conservation of matter must be considered to be an **exact law**. Whether it holds exactly for reactions in which there is considerable evolution of heat, such as the combustion of phosphorus, cannot be stated, since no experiments have been made with sufficient accuracy in these cases.

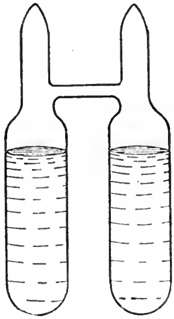


FIG. 22.—Landolt's Experiment.

Elements and compounds.—Homogeneous materials may undergo chemical changes in one of two ways, according to their composition. Either the substance **increases in weight** in all the changes which it undergoes ; or it gives other substances, each of less weight than the original substance, or, as is said, **decomposes.**

EXPT. 19.—Heat 0·5 gm. of magnesium ribbon in a weighed, loosely closed, porcelain crucible, with a small flame, till combustion ceases (Fig. 23). Then heat strongly for ten minutes, cool, and reweigh. There is an *increase in weight*, which, if the experiment is performed carefully, amounts to 0·333 gm.

EXPT. 20.—Heat 2·16 gm. of red oxide of mercury in a weighed, hard glass tube, connected by a rubber stopper with a glass delivery tube leading to a pneumatic trough in which is inverted a 200 c.c. measuring cylinder full of water, the mouth of which is over the delivery tube (Fig. 24). The red substance blackens, and bubbles of gas collect in the cylinder. At the same time, a shining metallic sublimate of mercury collects on the cooler part of the hard glass tube, which is supported in a horizontal position to prevent the globules of mercury which condense running back on to the hot glass. When the evolution of gas ceases and the oxide has disappeared, remove the delivery tube from the trough and allow the apparatus to cool. Reweigh the tube, and note that it has lost in weight. If the experiment has been carefully performed the *loss in weight* should amount to 0·160 gm. The volume of gas collected will be about 118 c.c. If a glowing chip of wood is placed in the gas, it is rekindled, and burns with a brilliant flame, indicating that the gas is **oxygen.**

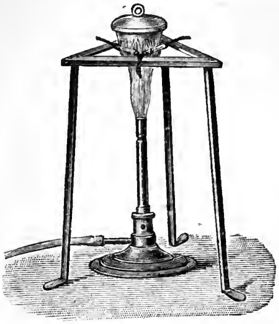


FIG. 23.—Heating Magnesium in Air.

If a pure substance can be decomposed into two or more substances of smaller weight, as the red oxide of mercury into mercury and oxygen gas, we say that it is a **Compound.** If it always yields substances of greater weight, indicating that, in all reactions in which it takes part, union always occurs with other substances, and never decomposition into two or more substances, the substance is called an **Element.** Magnesium is an element.

At this point, however, we meet again with a difficulty encountered in Chapter I, viz., that in some cases a homogeneous material may have a whole range of compositions according to the way in which it is prepared. Solutions of common salt in water may vary in composition from pure water to a liquid containing 26·5 per cent. by weight of salt. Between these two limits there is an infinite number of possible compositions. But if we decompose red oxide of mercury, no matter how it has been prepared (p. 26), we find that it always has the same composition, containing 8 gm. of oxygen to 100 gm. of mercury.

It is therefore necessary to divide into two classes all those homogeneous materials which are not elements. Those of constant composition are called **Compounds**; those of variable composition are called **Solutions.** Red oxide of mercury is a compound, but the liquids containing salt and water are solutions.

Solutions are sometimes called "Mixtures," but this name we have reserved for heterogeneous systems, *i.e.*, "Mechanical Mixtures," and it is therefore important to avoid confusion, by restricting the use of the word.

Solutions are always separable, by suitable means, into two or more **pure substances,** either elements or compounds. Thus, solutions of salt in water are separated into these two constituents by simple evaporation.

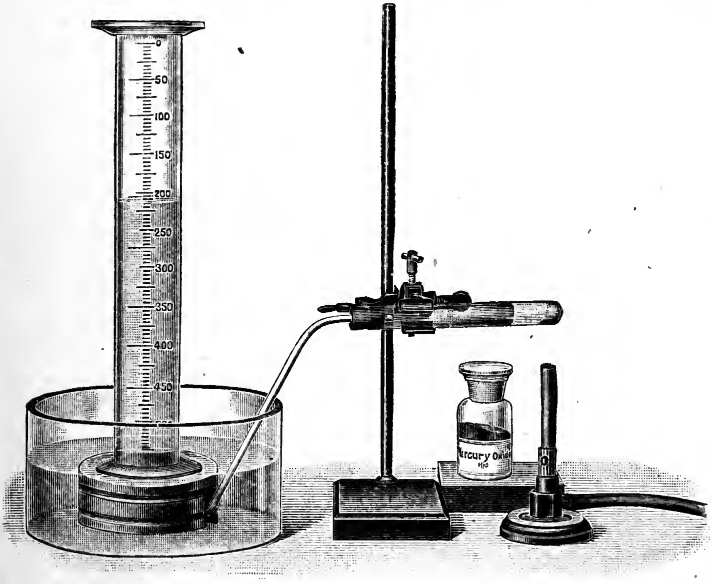
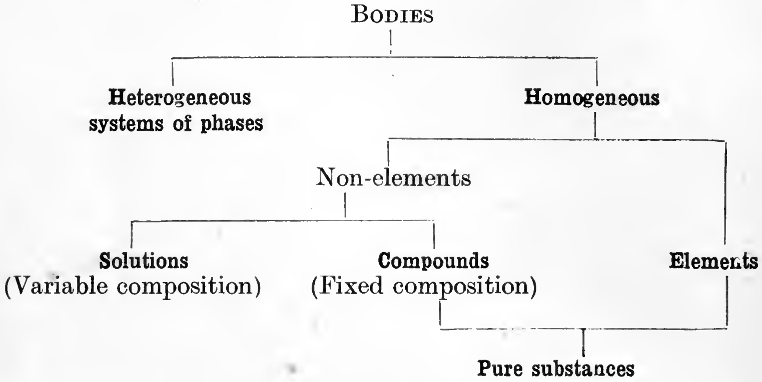


FIG. 24.—Decomposition of Oxide of Mercury by Heat.

In the above classification we remove the second difficulty encountered in the definition of pure substances (p. 6). The homogeneous liquids formed from salt and water, for instance, are not to be placed in separate groups of substances, the number of which would then be infinite, but are to be regarded as solutions of *two* pure substances, viz., salt and water, in varying proportions.

We have now arrived at the following classification :



Analysis and synthesis.—The process by which a compound is separated into its constituent elements, *e.g.*, the decomposition of red oxide of mercury by heat, is called **analysis**, from the Greek *analuo*, I unloose. The building up of a compound from its elements, as in the production of magnesium oxide by heating magnesium in air, is called **synthesis**, the Greek word *synthesis* meaning a putting together. The process of ascertaining the composition of substances is also called analysis; **qualitative analysis** leads to a knowledge of the constituents only, without finding the proportions in which they are combined, whilst **quantitative analysis** determines these proportions in addition.

It follows from the definition of a compound that its composition is independent of the method of preparation. The same compound, also, gives the same elements in the same proportions, no matter what means are used for its decomposition.

EXPT. 21.—Metallic tin may be converted into oxide of tin in three different ways :

(*a*) One gm. of tinfoil is weighed into a counterpoised Rose's crucible (Fig. 25), and heated in a stream of oxygen passed through the porcelain tube through a small hole in the lid of the crucible. The crucible is cooled and weighed from time to time until its weight becomes constant. The residue is oxide of tin.

(*b*) One gm. of tinfoil is weighed into a counterpoised porcelain basin, covered with a large watch-glass. It is treated carefully with successive small amounts of strong nitric acid until the violent action ceases, the watch-glass being placed over the basin after each addition to prevent loss by spirting. The solid on the glass is washed into the dish, and the excess of acid is then evaporated off on a sand-bath, and the material heated for ten minutes over a Bunsen flame. The dish is cooled and weighed. The residue is oxide of tin.

(*c*) One gm. of tinfoil is weighed into a conical flask and dissolved in strong hydrochloric acid by warming on a sand-bath. The solution of chloride of tin is diluted with water, and precipitated with a stream of sulphuretted hydrogen. The tin sulphide is filtered and washed, and the filter paper and precipitate ignited in a weighed porcelain crucible. This is cooled and weighed. The residue is oxide of tin.

It will be found that, within the limits of experimental error, the weight of oxide of tin obtained from 1 gm. of tin in the three different methods is the same. Hence the composition of oxide of tin is constant, and independent of the method of preparation. Oxide of tin is, therefore, a **compound**, not a mixture or a solution.

The early history of chemistry.—The conceptions underlying the definitions of elements and compounds, although now almost obvious, were reached only after centuries of effort. They represent the few grains of truth remaining from the winnowing process of experimental investigation applied to the mass of opinions on the constitution of bodies which had accumulated, either as a heritage from antiquity, or from the equally unverified guesswork of the later alchemical period. It may therefore not be out of place to give a very brief account of the development of these fundamental conceptions from the dawn of chemistry, one of the oldest of the sciences.

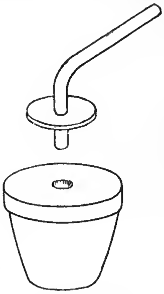
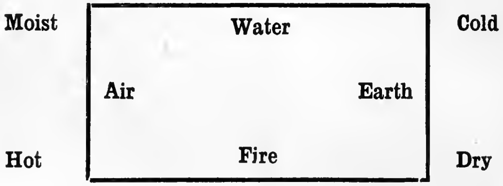


FIG. 25.
Rose's Crucible.

The definition of an element given above dates from the seventeenth century, when Robert Boyle, in his "Sceptical Chymist" (1661), agrees to use "elements and principles as terms equivalent, and to understand both by the one and the other, those primitive and simple bodies of which the mixed ones are composed, and into which they are ultimately resolved." According to Boyle, therefore, the **elements are the practical limits of chemical analysis**, or are substances incapable of decomposition by any means with which we are at present acquainted. This definition is provisional: substances now regarded as elements may, at some future date, with improved methods, be shown to be compounds, but until that happens they must be regarded as elementary.

Theory of the four elements.—The first clear expression of the idea of an element occurs in the teachings of the Greek philosopher, Aristotle (B.C. 384-322), who appears to have borrowed it from earlier thinkers of antiquity. All substances were considered to be made of a **primary matter,** called *hule.* On this, different **forms** could be impressed, much as a sculptor can make different statues from one block of marble. These forms can be removed, and replaced by new ones, so that the idea of the **transmutation of the elements** arose. Aristotle's elements are therefore really **fundamental properties** of matter, and as the most fundamental he chose hotness, coldness, moistness, and dryness. By combining these in pairs, as shown in the diagram, he obtained what are called the **four elements,** fire, air, earth, and water :



Thus, water is the type of moist and cold things ; fire of hot and dry, and so on. To the four material elements a fifth, immaterial, one was added, which appears in later writings as the **quintessence.** This corresponds with the modern **ether.**

Early alchemy.—The science of Chemistry arose from two sources :

1. The speculative philosophy of the Greeks.
2. The Egyptian art of working in metals.

The name Chemistry occurs later, and is supposed to be derived from the word *chemi*, meaning " black or burnt," or " Egyptian," or both.

The Egyptian technique, handed down from the workshops, was first described in Greek, and afterwards translated into Latin. Thus, in the **Papyrus of Leyden,** discovered at Thebes, and preserved in the Museum at Leyden, we find many practical recipes. This papyrus is written in Greek, at a date not accurately known but supposed to be the third century, and appears to have included the working notes of a fraudulent goldsmith. Recipes for *plating* base metals with gold occur in it, but the author is quite aware that no real transmutation had occurred. Thus, he says :

> " One powders up gold and lead into a powder as fine as flour, 2 parts of lead for 1 of gold, and having mixed them, works them up with gum. One covers a copper ring with the mixture ; then heats. One repeats several times until the object has taken *the colour.* It is difficult to

detect the fraud, since the touchstone gives the mark of true gold. The heat consumes the lead but not the gold."

In the course of translation of such documents, the language became confused, and the idea of a real transmutation crept in. On the conquest of Asia, Africa, and part of Europe, by the Arabs, the latter assimilated the knowledge of the subject races, and the study of chemistry was called Alchemy, the prefix *al* being the definite article in Arabic. Further translations were made, and additional errors arose.

Geber.—Geber was an Arabian alchemist living in the ninth century, but the Latin * writings usually attributed to him belong to a much later date. The "Latin Geber" added to the four elements of Aristotle the **alchemical elements, sulphur,** and **mercury**; a third, **salt,** was introduced by another alchemist called Basil Valentine, supposed to have written in 1470, but probably mythical, the real author being a German, Thölde, living in the seventeenth century.† Sulphur was the principle of combustibility; salt the fixed part left after calcination; whilst mercury was the principle of metallicity, contained in all metals.

Gold and silver, according to the Latin Geber, contain a pure mercury, united with a "clean sulphur," which is red in the gold and white in the silver. Other metals contain an "unclean sulphur," but it was supposed that the base metals could be converted into gold and silver by altering the proportions of mercury and sulphur in them and "cleansing" the latter. This process was to be brought about by a substance called the **philosopher's stone,** which was described as a red powder. Some of the recipes for its preparation, in so far as they are intelligible, show that it was an amalgam of gold, or a solution of gold in mercury, the latter being driven off in the fire, leaving the gold.

Iatrochemistry.—In the sixteenth and seventeenth centuries another school of chemists arose, called the **Iatrochemists,** *i.e.*, the **medical chemists,** who attempted to prepare the **elixir of life,** which should cure all diseases, and confer perpetual youth. Paracelsus (1493–1541) was the founder of this sect; he believed in the philosopher's stone and the elixir of life. It was thought that the philosopher's stone and the elixir of life would, when prepared, turn out to be the same, an idea which no doubt arose partly from the Oriental imagery of the Arabian alchemists, who spoke of "healing" metals when they were transmuted, and partly because many substances, such as arsenic, mercury, and zinc, change the

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* "Liber Geber," British Museum, 1473 (?). English translation: "The Works of Geber, the Most Famous Arabian Prince and Philosopher," Richard Russel, London, 1678.

† *Triumph Wagen antimonii*. F. Thoelde, Leipzig, 1604.

colours and properties of metals and also have a powerful action on the human body.

Experiments on the supposed transmutation included the roasting of the sub-metallic mineral galena in air, when lead was formed, with a strong smell of sulphur; and the production of a small button of silver when the lead was burnt off by heating on a cupel, or dish made of bone-ash. Also, if iron pyrites, a yellow mineral looking somewhat like gold, was melted with lead, and the lead cupelled, a minute amount of gold was left. Both the silver and gold, of course, pre-existed in the minerals, and are prepared from them at the present day. Again, a steel knife-blade dipped into a solution of blue vitriol (copper sulphate) apparently became converted into copper.

The later history of Alchemy, however, is mainly that of fraud practised by the "adepts" on credulous dupes, so that the "science" ended as it began. One method of effecting transmutation was to stir the materials in the crucible with a hollow iron rod filled with gold powder, and stopped with wax.

Attempts at transmutation have been made in quite recent times, the philosopher's stone in this case being **radium.** Ramsay and Cameron (1907) thought they had converted copper into lithium to a minute extent by exposing a solution of copper sulphate to the emanation of radium, but Mme. Curie showed that the lithium came from the quartz vessels used.

Van Helmont (1577–1644) represents the transition from alchemy to modern chemistry. His writings * show the beginnings of scientific method, although he still believed in transmutation, having seen the operation performed once by an adept, and sought for the *alkahest*, or universal solvent. He considered that all materials were derived from water, as taught by Thales (B.C. 600), and describes an experiment in which a small willow twig was grown in a weighed pot of earth, supplied only with water. After five years the tree was weighed, and had gained 164 lb. in weight, whereas the earth had lost practically nothing. Hence he concluded that the tree had been formed solely from water.

It is something of an irony of fate that this erroneous conclusion, in which the assimilation of carbon dioxide from the air by the plant was ignored, should have been reached by the discoverer of that gas. Van Helmont invented the name **gas**, derived from *chaos*, describing the supposed wild motion of its particles, and designated carbon dioxide as *gas sylvestre*, *i.e.*, the "gas of the woods," or the "wild, untamable gas," because, having corked up limestone and acid in a bottle, he found that the latter was burst by the gas

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* "Ortus Medicinae," Amsterdam, 1648; Leyden, 1656.

sylvestre. A gas, according to Van Helmont, is something which cannot be kept in a vessel.* In his treatise "de Flatibus" he mentions another gas, *gas pingue*, which is inflammable, and is produced in fermentation. It was probably impure hydrogen.

Robert Boyle.—Modern chemistry may be said to have begun with Robert Boyle (1627–1691), and for two reasons. In the first place Boyle was the first to study chemistry for its own sake, and not as a means of making gold or medicines. In the second place, he introduced a rigorous experimental method into chemistry, and in particular overthrew the doctrines of the Aristotelian and Alchemical elements, by showing that none of them could by any process be extracted from metals. In the case of gold, neither

Robert Boyle.

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* "Hunc spiritum incognitum hactenus, novo nomine *gas* voco, qui nec vasis cogi, nec in corpus visibile reduci potest."

water nor solvents can extract sulphur or mercury from it: "the metal may be added to, and so brought into solution or crystalline compounds, but the gold particles are present all the time, and the metal may be reduced to the same weight of yellow, malleable, ponderous substance as it was before the experiment." Boyle's definition of an **element** has already been given (p. 27).

The chemical elements.—The list of substances at present accepted as elements, which is given on p. 145, comprises eighty-six names. Of these only about one-half are those of substances commonly found in chemical laboratories, and of these only about twenty occur in the uncombined state. About 99 per cent. of terrestrial matter is composed of some twenty elements and their compounds.

An estimate of the **occurrence of the elements** in the air, the sea and other waters, and the crust of the earth to a depth of twenty-four miles, has been made by F. W. Clarke. The following table gives the average composition by weight of these materials, taken together, in parts per 100:—

Oxygen	49·85	Calcium	3·18	Hydrogen	0·97
Silicon	26·03	Sodium	2·33	Titanium	0·41
Aluminium	7·28	Potassium	2·33	Chlorine	0·20
Iron	4·12	Magnesium	2·11	Carbon	0·19

Oxygen is seen to be the most abundant element, accounting for one-half the total mass; silicon, which occurs mainly in the form of the oxide silica as quartz and sand, and in combination in many rocks, is the next in abundance. Nitrogen, occurring in the atmosphere, and the other elements, many of them constituting living matter, together equal only about 1 per cent. of the whole.

The composition of the centre of the earth is not accessible to experiment, but since the mean density of the earth is about 5·6, the central part must consist largely of substances of high density, one of which is probably iron.

Some of the elements are widely distributed in nature, some in large quantities, such as oxygen, silicon, sodium, and iron, and others in very much smaller amounts, such as lithium, rubidium, and helium. Other elements, such as erbium, occur only in very small amounts in particular localities.

By means of **spectrum analysis** (Chap. XXXVI), it is possible to discover the elements present in the **sun and stars.** The following elements have been recognised in the atmosphere of the sun: aluminium, barium, beryllium, cadmium, calcium, carbon, cerium, chromium, cobalt, copper, erbium, germanium, helium, hydrogen, iron, lanthanum, lead, magnesium, manganese, molybdenum, neodymium, nickel, niobium, oxygen, palladium, rhodium, scandium, silicon, silver, sodium, strontium, tin, titanium, vanadium, yttrium, zinc, zirconium, and nitrogen as cyanogen. The following are doubtful: iridium, lithium, osmium, platinum, potassium, ruthenium, tantalum, thorium, tungsten, and uranium.

The spectra of stars show that these may be divided into groups. Some stars show dark lines on a bright spectrum ground; others show bright lines on a faint spectrum background. Great differences are found in the stellar spectra, and the classification usually adopted by astronomers is as follows:

Class O (Wolf-Rayet type): bright lines on a faint continuous background.

Class B (Orion type): dark lines of helium sparsely set on a bright ground.

Class A (Sirian type): hydrogen lines most conspicuous.

Class F (Calcium type): hydrogen lines still conspicuous, but many faint lines of metals appear, notably two strong calcium lines in the violet.

Class G (Solar type): numerous strong metallic lines appear, as in sunlight.

Class K (Sun-spot type): lines darker, and flutings occur, as in sunspots. Hydrogen lines faint.

Class M (Fluted type): flutings due to titanium oxide marked, as well as flutings due to carbon.

The **nebulæ** show the presence of hydrogen, helium, and possibly an element, *nebulium*, not known on the earth.

Lockyer observed that the hotter stars contain fewer elements than the cooler stars, and he assumed that some of the terrestrial elements are decomposed at the very high temperatures in the hot stars into simpler elements, some of which may be the ordinary elements known to us.

Specimens of extra-terrestrial elements come to us occasionally in the form of **meteorites**, which are masses consisting chiefly of metallic iron, together with nickel, phosphorus, carbon, oxygen, calcium, silicon, and hydrogen. No new elements are found in them.

On the whole, therefore, we may assume that the composition of the sun and stars is similar to that of the earth, or still simpler.

SUMMARY OF CHAPTER II

All parts of a homogeneous pure substance exhibit the same properties, and behave in the same way, under the same conditions. Pure substances may become changed into other pure substances, with different properties. This is the result of **chemical change.** These changes may be proved experimentally to depend on the **combination** of forms of matter previously distinct, or the separation of distinct substances from a previous condition of union, *i.e.*, to **decomposition.** Pure substances, after having undergone chemical change, may be recovered, qualitatively and quantitatively the same as they were at first, by a reverse process of change. This is a result of the **Law of Conservation of Matter,** or the **Law of Indestructibility of Matter.**

Certain substances have resisted all attempts to decompose them, and in the present state of our knowledge are regarded as **chemical elements,** or the simplest distinct forms of matter.

(See Mallet, "Memorial Lecture on Stas," Chemical Society's *Memorial Lectures*, 1893.)

EXERCISES ON CHAPTER II

1. Define: compound, element, solution, analysis, synthesis, chemical change. In what ways does a chemical change differ from a physical change ?

2. State the Law of Conservation of Matter, and describe two simple experiments to illustrate its application to chemical changes. To what degree of accuracy is it known to be true, and how has this been tested ?

3. Trace briefly the evolution of the conception of the chemical elements. What is known as to the distribution of the elements in the earth and stars ?

4. On what theoretical and experimental bases was Alchemy founded, and why has its pursuit been abandoned by chemists ?

5. Why are common salt and water said to be compounds, but the liquid formed by mixing them together a solution ?

CHAPTER III

THE COMPOSITION OF THE AIR AND THE THEORY OF COMBUSTION

The discovery of gases.—Reference has been made to the two gases described by Van Helmont (1577–1644), viz., *gas sylvestre* (carbon dioxide) and *gas pingue* (hydrogen). No new gases were discovered from then until the time of Priestley (1772), although the two gases of Van Helmont were carefully investigated by Henry Cavendish (1766); gas sylvestre was named **fixed air** by Joseph Black, 1755, and gas pingue **inflammable air** by Cavendish, respectively. Inflammable air was obtained by the action of sulphuric and hydrochloric acids on zinc, iron, and tin. Cavendish observed that the inflammable air was "the same, and of the same amount, whichever acid is used to dissolve the same weight of either metal" [iron or zinc], and hence concluded that the gas came from the metal. He found that inflammable air was much lighter than common air, whilst carbon dioxide was heavier. ("On Factitious Airs," *Phil. Trans.*, 1766.)

Joseph Priestley (1733–1804), whose discoveries are recorded in his "Observations on Different Kinds of Air," * recognised several new gases. At that time gases were called "airs," Van Helmont's name, **gas**, having dropped out of use. Priestley prepared and examined oxygen, nitrous oxide, nitric oxide, nitrogen dioxide, hydrochloric acid gas, ammonia gas, and sulphur dioxide. He improved the familiar **pneumatic trough**, and was able to collect over mercury many gases which are very soluble in water (*e.g.*, ammonia, and sulphur dioxide).

Priestley's work firmly established the fact that a number of different gaseous forms of matter exist, each with definite properties, so that the old idea that such of these as had been noticed were merely common air mixed with impurities, was finally abandoned.

Combustion and the calcination of metals.—There are two kinds of chemical change which, since they were investigated side by side,

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* 6 vols., 1774–86; abridged edition, 3 vols., 1779–86.

and depend on the same cause, may conveniently be described together. These are **combustion,** and the **calcination of metals.**

The alchemists attached great importance to the effects of heat on substances, and their writings describe many types of furnaces, and experiments made with them. The metals, except gold and silver, were found to change when heated in open crucibles, and to leave a dross, which was called a **calx** (Latin *calx*, lime). It was noticed in the sixteenth century that this calx is heavier than the metal: the explanation usually given was that fire, or **caloric,** possessed weight, and was absorbed by the metal in forming the calx. Jean Rey (1630) " devoted several hours to the question," without apparently making any experiments, and concluded that the **air** becomes thickened or adhesive by the action of the fire, and sticks to the metal. His ideas are very crude and inaccurate.

Nitre air.—Robert Boyle * (1673) heated tin in a glass retort, and when it was melted, sealed off the neck and continued the heating for two hours. The retort was cooled, and the sealed tip of the neck broken. Air rushed in, " because when the retort was sealed, the air within it was highly rarefied." Boyle, from his method of experimenting, therefore did not notice, as Lavoisier did a century later, that some of the air was absorbed, and that the tin had increased in weight.

Boyle then showed that when sulphur was sprinkled on a red-hot plate under an exhausted air-pump receiver, it smoked but did not burn. On admitting air, " divers little flashes were seen." But if gunpowder were sprinkled on the hot plate under the vacuous receiver, he saw " a pretty broad blue flame, like that of brimstone, which lasted so long as we could not but wonder at it." Gunpowder could also burn under water. Boyle, therefore, somewhat reluctantly, concluded that *a flame can exist without air,* and that the increase in weight of metals on calcination is due to their absorption of caloric, or fire, which he considered to be material, and capable of being weighed in a balance. He observed that if charcoal is strongly heated in a closed retort it does not burn, but the *caput mortuum* (a fanciful name due to the alchemists, who represented a **residue** by the symbol of the skull and crossbones) becomes black again on cooling. If, however, air is admitted, the charcoal burns, and crumbles down to white ashes.

The latter experiment was repeated by Robert Hooke (at one time an assistant to Boyle), who, in his " Micrographia " (1665), put forward the first rational **theory of combustion.** Hooke found that a bit of charcoal or sulphur burns brilliantly when thrown into fused nitre.

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* Works, edited by Birch, 5 vols., 1744; abridged by Boulton 4 vols., 1699–1700; do. by Shaw, 3 vols., 1738.

Expt. 22.—Fuse about 5 gm. of nitre in each of two test-tubes, supported by clamps over a tray of sand. Throw into one a small piece of charcoal; this swims about and burns brightly. Into the other throw a *small* piece of sulphur: this burns with a beautiful blue flame.

On the basis of these experiments Hooke founded his theory of combustion, which was briefly as follows:

"(1) Air is the universal dissolvent of all sulphurous [*i.e.*, combustible] bodies. (2) This action of dissolution produces a very great heat, and that which we call *fire*. (3) This dissolution is made by a substance inherent and mixed with the air that is like, if not the very same with, that which is fixed in saltpetre [nitre]." This substance he called **nitre air.** In this way he was able to explain the combustion of gunpowder, one constituent of which is nitre, in the absence of air.

John Mayow ("Tractatus quinque medico-physici," Oxford 1674) elaborated a theory similar to that of Hooke, but supported by descriptions of experiments (which were not published by Hooke). He concluded that **air consists of two gases**; one is the nitre-air of Hooke, called by Mayow *spiritus nitro-aëreus*, which is concerned in combustion and respiration; and the other is an air incapable of supporting either of the latter.

The experimental evidence was as follows:—

(1) Expt. 23.—Mayow inverted a large glass globe over a lighted candle standing in water, equalising the levels of the latter by means of a siphon, which was then quickly withdrawn. The water rose inside the globe, showing that some air had disappeared. When the candle was extinguished, a large bulk of air was left, but this would not support the combustion of sulphur or camphor lying on a small shelf inside the globe, when they were heated by a burning glass. (Fig. 26.)

(2) A mouse when introduced into the residual gas died. Conversely, when a lighted candle was plunged into a confined volume of air in which a mouse had died it was instantly extinguished. If a mouse was kept in a vessel of air closed by a bladder (Fig. 27), the contraction of the air was perceptible.

(3) Gunpowder rammed into a paper tube and ignited continued to burn under water. The air fixed in nitre can therefore take the place of ordinary air in supporting combustion, and since things burn more brilliantly in fused nitre than in common air, the nitre must contain an abundant supply of nitre air, which is the part of common air concerned in combustion.

(4) Mayow repeated an old experiment described in Libavius' "Alchymia" (1595), viz., calcining a cone of metallic antimony on a

marble slab by means of a burning-glass. Although abundant fumes were evolved, the calx weighed more than the metal. The calx was found to be identical with that formed by the action of nitric acid on the metal.

Mayow did not succeed in isolating nitre air, and although Hooke, in his "Lampas" (1677), says that his theory was generally received (a similar theory was in fact mentioned by Lemery in his "Cours de Chemie," 1675), these beginnings of a true theory of combustion were soon stifled by an erroneous dogma, due to two German chemists, which persisted for a century, and obscured nearly every branch of chemical science. This was the famous **theory of phlogiston,** of Becher and Stahl.

Theory of phlogiston.—It was a favourite expression of the alchemists that inflammable bodies contain **sulphur**: *ubi ignis et calor ibi sulphur.* John Joachim Becher, in his "Physicæ subterraneæ" (1669), remarked that the constituents of bodies are air, water, and three earths, one of which is *inflammable* (*terra pinguis*); the second *mercurial*; the third fusible, or *vitreous.* These correspond with the sulphur, mercury, and salt of the alchemists. On combustion, the "fatty earth" burns away.

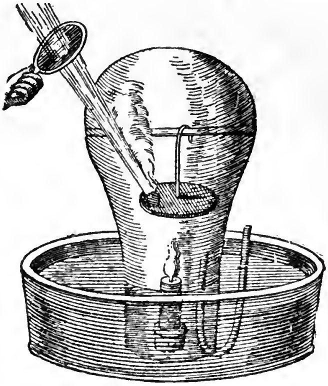

FIG. 26.—Mayow's Experiment on Combustion.

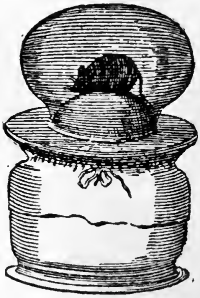

FIG. 27.—Mayow's Experiment on Respiration.

In 1702 Becher's treatise was republished, with a long introduction, by George Ernst Stahl, professor at Halle. Stahl was a good chemist and an excellent teacher, and in his lectures and text-book ("Fundamenta chymiae," 1723), he popularised Becher's views in an improved form. He gave the name **phlogiston** (from the Greek φλόξ = flame) to the *terra pinguis* of Becher. When bodies burn, or are calcined, phlogiston escapes with a rapid whirling motion; when the original bodies are recovered by reduction, phlogiston must be replaced. Oil, wax, charcoal, and sulphur are all rich in phlogiston, and may be used to restore it to a burnt material. Zinc on heating to redness burns with a brilliant flame, hence phlogiston (ϕ) escapes. The white residue is calx of zinc. If it is heated to whiteness with charcoal (rich in phlogiston) zinc distils off. Hence: **calx of zinc** $+ \phi =$ **zinc.** Similarly with other metals. If phosphorus is burnt, it produces an acid matter, and much heat and light are evolved. Hence: **phosphorus** $=$ **acid** $+ \phi$. If the acid is heated with charcoal, phlogiston is absorbed and phosphorus is reproduced.

Stahl's theory united a great many previously isolated facts, and became almost universally accepted during the eighteenth century. During this period the increase in weight of metals on calcination was usually ignored as of little importance, or as belonging to physics rather than to chemistry, although the fact was destined later to overturn the whole theory of phlogiston.

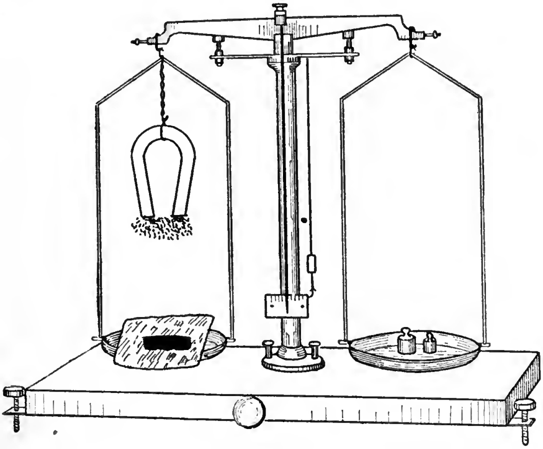

Fig. 28.—Increase in Weight of Iron on Burning.

Expt. 24.—This increase of weight is readily shown by the following experiment. Some finely divided *reduced iron* is taken up by a horse-shoe magnet counterpoised from one arm of a sensitive balance (Fig. 28), a piece of asbestos paper being placed in the pan underneath the magnet. If a spirit-lamp flame is applied to the tufts of iron adhering to the magnet, the powder begins to glow, and after calcination falls from the magnet. The pan on the side of the balance where the magnet is suspended sinks, showing that the iron increases in weight during calcination. The iron calx left is found to be black in colour, whereas the original iron powder is grey.

Scheele's experiments on fire and air.—Carl Wilhelm Scheele (1742–1786) was a firm believer in Stahl's theory. A poor apothecary of Stockholm, he made a great number of chemical discoveries of the very first rank, those on combustion being published in his treatise "On Air and Fire." These experiments were made chiefly before the autumn of 1770, and all prior to 1773. The MS. reached the printers in 1775, but owing to delay the book did not appear until 1777, when many of Scheele's discoveries had been made independently, and published, by Priestley in England. Scheele's priority was only established in 1892, from his original laboratory notes, discovered at Stockholm.

In his first set of experiments Scheele noticed the contraction of a confined volume of air standing in contact with various materials. He used, for instance, a solution of liver of sulphur (*hepar sulphuris*), a solution of sulphur in lime-water, linseed oil, and iron filings moistened with water, all of which, he observes, are rich in phlogiston, or, as he called it, the **inflammable substance**. In all cases there was a **loss of air**.

A solution of sulphur in potash, which is yellow, became colourless in contact with air, and the solution contained "vitriolated tartar," which could be formed from potash and sulphuric acid. No sulphur was left over.

Expt. 25.—Take three glass tubes, 2 ft. long and $\frac{3}{4}$ in. wide, fitted with rubber stoppers, and divided into five equal volumes by strips of label. In one place a moistened piece of liver of sulphur (made by fusing potassium carbonate with flowers of sulphur in a covered crucible till evolution of gas ceases), and in the second a piece of phosphorus stuck on a piece of copper wire. Wet the inside of the third tube with water, and sprinkle it with clean iron filings. Cork the three tubes and allow them to stand inverted in three large glass cylinders of water for a few days (Fig. 29). Open the tubes under water, and observe that the latter rises in the tubes until one-fifth of the volume is occupied. Cork the tubes, remove them from the cylinders, and insert a lighted taper into the gas in each. The flame is extinguished.

The inflammable substance was not contained in the residual gas, which differed from common air. For, if this gas had been formed by the union of common air with phlogiston, and contraction, it should be denser than common air. But: "a very thin flask which was filled with this air, and most accurately weighed, not only did not counterpoise an equal volume of ordinary air, but was even somewhat lighter." Thus, "the **air is composed of two fluids**, differing from each other, the one of which does not manifest in the least the property of attracting phlogiston, whilst the other, which composes between the third and fourth part of the whole mass of the air, is peculiarly disposed to such attraction." These two constituents of common air Scheele called **Foul Air**, and **Fire Air**, respectively.

Scheele next placed a little phosphorus in a thin flask, corked the latter, and warmed it until the phosphorus took fire. A white cloud was produced, which attached itself to the sides of the flask in white flowers of "dry acid of phosphorus." On opening the flask under water, the latter rushed in, and occupied a little less than one-fifth of the flask [EXPT. 26]. By allowing phosphorus to stand for six weeks in the same flask, until it no longer glowed, about one-third of the air was lost.

Scheele then burnt a hydrogen flame under a glass globe standing over water (Fig. 30). The water at once began to rise, until it filled one-fourth of the flask, when the flame went out.

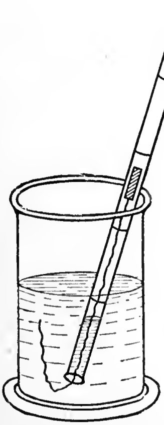

FIG. 29.—Diminution of Air by Phosphorus.

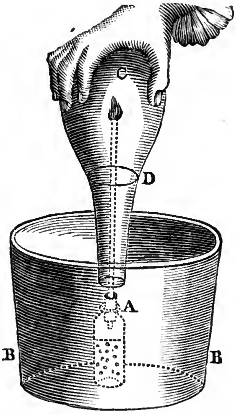

FIG. 30.—Scheele's Experiment on the Combustion of Inflammable Air.

EXPT. 27.—Burn a jet of hydrogen from a Kipp's apparatus (p. 185) inside a graduated bell-jar over water. The gas is turned off as soon as the flame goes out, and, after cooling, it will be found that one-fifth of the air has disappeared (Fig. 31).

Scheele thought that hydrogen (inflammable air) was phlogiston, and in considering the last experiment he asked himself:

(1) What has become of the fire air?

(2) Where has the phlogiston (inflammable air) gone?

The fire air, he argued, must either remain in the air, be dissolved in the water, or have escaped through the vessel. (He did not notice the *moisture* condensed on the flask, which contained both the missing gases, because he worked over hot water, which itself gave off steam.) The residual foul air was lighter than common air, although the latter had undergone a contraction, hence the two substances cannot be present in it. Further, he found nothing in the water. Scheele therefore concluded that the fire air and phlogiston had escaped through the glass, combined in the form of heat and light, which he considered to be material and called **caloric: fire** (or **caloric**) = **fire air** + ϕ.

This hypothesis, of course, is quite incorrect, but it led Scheele to the most important discovery that has ever fallen to the lot of a chemist, viz., **the isolation of "fire air."** It is by no means uncommon to find an important discovery resulting directly from a false assumption.

Scheele now set himself to reverse the change he thought had taken place, *i.e.*, to decompose caloric (or heat) into fire air and phlogiston. For this purpose it was necessary to present to the caloric a substance having a greater attraction for phlogiston than is exhibited by fire air. The latter should then be set free. For this substance he chose *nitric acid*, because it readily corrodes metals, taking out their phlogiston, and forming red fumes. In order to subject it to the action of caloric, the acid must be fixed, and Scheele did this by combining it with potash. In order to set the acid free again at the high temperature, he distilled the resulting nitre with strong oil of vitriol (sulphuric acid) in a retort (Fig. 32). Brown fumes came off, which were absorbed in a bladder containing milk of lime, attached to the neck of the retort. The bladder gradu-

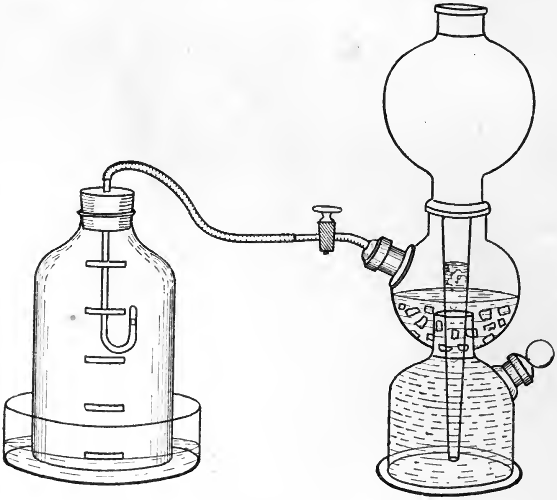

FIG. 31.—Combustion of Hydrogen in Air.

ally filled with a colourless gas, in which a taper burned with a flame of dazzling brilliance. This was **fire air**—the "nitre-air" which had eluded Hooke and Mayow.

Scheele prepared fire air in a variety of other ways. Thus, he heated calx of mercury (*mercurius calcinatus per se*), which he supposed absorbed phlogiston from the caloric, setting free the fire air :

$$\textbf{Calx of Mercury} + \underbrace{(\phi + \textbf{Fire Air})}_{\textbf{Caloric}} = \underbrace{(\phi + \textbf{Calx of Mercury})}_{\textbf{Metallic Mercury.}} + \textbf{Fire Air.}$$

He also obtained fire air by heating :

(1) Black manganese (manganese dioxide) with sulphuric or arsenic acid [Expt. 28].

(2) Nitre alone strongly. This gives fire air, and a residue evolving red fumes with acid [Expt. 29].

(3) Silver or mercurous carbonate, the *aerial acid* (carbon dioxide) simultaneously produced being absorbed by means of an alkali : silver carbonate = silver + fire air + aerial acid.

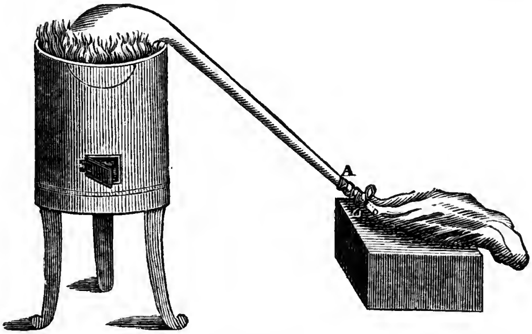

Fig. 32.—Scheele's Experiment: Isolation of Fire Air.

(4) Magnesium and mercurous nitrates [Expt. 30].

Scheele found that fire air is *completely* absorbed by moist liver of sulphur. When he burnt phosphorus in a thin flask of it, the flask burst on cooling. With a thicker flask, the cork could not be taken out under water, but could be pushed in, when water rushed in and filled the flask. A hydrogen flame continued burning in the gas until seven-eighths were absorbed.

When fire air was added to the foul air left after combustion of hydrogen, etc., in air, so as to restore the original volume, the mixture had all the properties of ordinary air, *e.g.*, it left the same residue after standing over liver of sulphur.

Expt. 31.—Fill a gas-jar, divided into 5 parts, four-fifths with nitrogen from a gas-holder, and then fill up the remaining one-fifth with oxygen. Test the gases separately in tubes with a taper, and then the mixture.

Scheele placed various animals and insects in confined volumes of air, taking care to put along with them their appropriate foods. He found that they ultimately died; *aerial acid* (Black's *fixed air*) was produced, and a contraction of the air resulted, the residue extinguishing a flame. Similar results were found with sprouting peas. Two large bees were placed in a bottle of fire air over milk of lime, Scheele having "provided some honey for their stay." After eight days the bottle was almost completely filled with liquid, and the bees were dead. He also noticed that the fire air is partly dissolved out of common air when this stands over water which had been boiled. A candle burns more brightly in the air expelled from the water by boiling than in common air.

JOSEPH PRIESTLEY.

Priestley's experiments on dephlogisticated air.—Priestley, having come into the possession of a powerful convex lens, or *burning-glass*, tried by its aid to extract "air" from various chemicals given to him by his friend Warltire. Among these was **red precipitate**, or *mercurius calcinatus per se*, obtained by heating mercury in air, the nature of which had long been a puzzle to chemists. The substances were heated by focussing the sun's rays on them in small phials (Fig. 33) filled with, and inverted over, mercury.

"Having procured a lens of twelve inches diameter, and twenty inches focal distance [the statue of Priestley at Birmingham, in which he is represented as performing his famous experiment, shows, in error, a very much smaller lens than this], I proceeded with great alacrity to examine, by the help of it, what kind of air a great variety of substances, natural and factitious [*i.e.*, *artificially* prepared: *cf.* Cavendish's *factitious airs*] would yield . . . With this apparatus, after a variety of other experiments, . . . on the 1st August, 1774, I endeavoured to extract air from *mercurius calcinatus per se*; and I presently found that, by means of this lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express, was, that a candle burned in this air with a remarkably vigorous flame . . . I was utterly at a loss how to account for it."

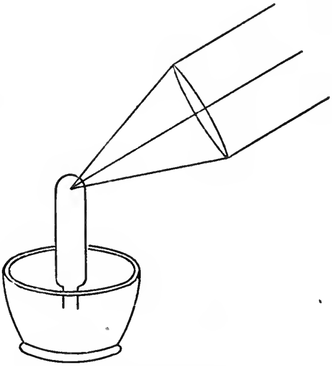

FIG. 33.—Isolation of Oxygen by Priestley (1774).

Priestley's haphazard method of work is clear from this quotation: in another place he remarks that in his discoveries "more is owing to what we call *chance*, that is, philosophically speaking, to the observation of *events arising from unknown causes*, than to any proper *design* or preconceived *theory* in this business."

Priestley found that a mouse lived twice as long in the new air as in the same confined volume of common air, and revived afterwards when taken out. He breathed it himself, and fancied his "breast felt peculiarly light and easy for some time afterwards"—hence he recommended its use in medicine (it is now used in the treatment of gas poisoning and pneumonia).

Priestley, who was a minister of religion, was doubtful whether we might not "live out too fast" in it, and remarks that: "The air which nature has provided for us is as good as we deserve." He suggested that by blowing fires with the new air, very high temperatures might be attained, and his friend Michell was later on able to melt platinum in this way.

Priestley now asked himself: "What is this new air?" He assumed, from the teachings of Stahl, that a candle on burning gives out phlogiston, and is extinguished in a closed vessel after a time because the air becomes saturated with phlogiston. Ordinary air, therefore, supports combustion because it is only partially saturated with phlogiston, and can absorb more of it. Substances burn in air with only a moderate flame, whereas in the new air the flame is vivid; Priestley, therefore, concluded that the new gas must contain little or no phlogiston, and hence he called it **dephlogisticated air.** The gas left when bodies burnt out in ordinary air was named, for a similar reason, **phlogisticated air**:

Phlogisticated Air [Nitrogen] = **Air** + ϕ. (Scheele's **Foul Air.**)
Dephlogisticated Air [Oxygen] = **Air** − ϕ. (Scheele's **Fire Air.**)

Priestley believed that "phlogiston is the same thing as inflammable air, and is contained in a combined state in metals, just as fixed air is contained in chalk and other calcareous substances; both being equally capable of being expelled again in the form of air [by the action of acids]."

Lavoisier and the Antiphlogistic Theory.—Antoine Laurent Lavoisier (1743–1794), the famous French scientist, began his experiments on **combustion** in 1772. He found that when sulphur and phosphorus are burnt in closed glass tubes they do so at the expense of part of the air, since

(*a*) if the tube be afterwards opened under water, the latter rushes in and partially fills the vessel;
(*b*) if opened in the air, the latter rushes in, and the vessel becomes heavier.

He concluded that both these **substances on burning take something from the air.**

Lavoisier next modified Boyle's experiment of calcining tin and lead, by using weighed *sealed* retorts. He obtained the same results as with sulphur and phosphorus, and drew the same conclusion. On heating the *calx of lead* with charcoal he found it lost in weight, and "an air was abundantly evolved." Thus something is taken from the calx in forming the metal, and this must be "an air." Further Lavoisier could not go.

But in October, 1774, Priestley visited Paris with Lord Shelburne, and told Lavoisier at dinner of his discovery of dephlogisticated air, saying he "had gotten it from *precip. per se* and also *red lead*"; whereupon, he says, "all the company, and Mr. and Mrs. Lavoisier as much as any, expressed great surprise." In Lavoisier's notebook of 1775 there occurs an entry dated 13th February, recording an experiment on "précipité *per se* de chez M. Baumé," and mentioning the disengaged gas as "l'air déphlogistique de M. Prisley" (*sic*). When, therefore, Lavoisier, in his "Traité de Chemie" (1789), speaks of "this air, which Dr. Priestley, Mr. Scheele, and I discovered about the same time," one is compelled to dissent. There is no evidence that Lavoisier had any claim to be regarded as a discoverer of oxygen gas.

LAVOISIER.

Lavoisier was quick to see the important bearing of Priestley's discovery on his own unfinished work; he was able to prove that it is **dephlogisticated air** which is absorbed in the calcination of metals, by a famous experiment, described in his "Traité" (1789).

He heated 4 oz. of mercury in a retort which communicated with a measured volume of air in a bell-jar over mercury (Fig. 34). The volume of air in the bell and in the retort was 50 cu. in. After a time he noticed the formation of red specks, and scales, of calx on the surface of the mercury. After twelve days the scales no longer increased; the fire was removed, and the experiment stopped. The air had contracted to 42 cu. in., and the gas left was "mephitic air," which Lavoisier at first called **atmospheric mofette.** The scales, or mercury calx (*mercurius calcinatus per se*), were collected and found to weigh 45 grains. They were transferred to a small retort and heated; 8 cu. in. of dephlogisticated air, which was "an elastic fluid, much more capable of supporting respiration and combustion than ordinary air," and hence called by Lavoisier **vital air,** or **air eminently respirable,** were obtained, together with 41½ grains of mercury. When this vital air was added to the atmospheric mofette, ordinary air was formed without any evolution of heat or light, hence air is probably simply a mixture of these two gases (as had previously been suggested by Scheele).

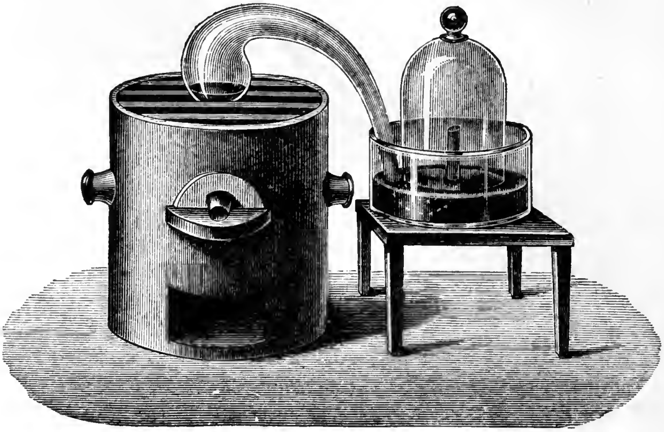

FIG. 34.—Demonstration of the Composition of Air by Lavoisier (1789).

Lavoisier made experiments on the combustion of substances in vital or "pure" air, and summed up his conclusions in the four statements:

(1) Substances burn only in pure air.

(2) Non-metals, such as sulphur, phosphorus, and carbon, produce **acids** on combustion; hence the gas was called **oxygen** (ὀξὺς = *acid*).

(3) Metals produce **calces** on absorption of oxygen.

(4) Combustion is in no case due to an escape of phlogiston, but to chemical combination of the combustible substance with oxygen.

These statements comprise the fundamental tenets of the **anti-phlogistic theory.**

Expt. 32.—Lavoisier's experiments may be repeated by burning sulphur, phosphorus, and carbon in jars of oxygen, the substances being held by deflagrating spoons, and shaking the products with litmus. The latter is reddened. Magnesium ribbon burns with a blinding light, giving a white calx, which turns moist red litmus paper blue.

Lavoisier's conclusions were not accepted at once; Black in England, and a few French chemists, supported them, but there was one great difficulty still to be overcome, viz., that the phlogistic theory could explain a set of experiments which the antiphlogistic theory could not. A metal like tin or zinc dissolves in an acid giving inflammable air, and a salt is left on evaporating the solution, which, on strong heating, parts with its acid and leaves the calx of the metal. The same salt is formed when the calx is dissolved in the acid, but no inflammable air is then evolved. Whence comes the inflammable air in the first experiment? This was an easy question for the phlogistonists. "**Inflammable air,**" said they, "is **phlogiston**; the **metal** is (**calx** + **phlogiston**); and the **salt** is (**calx** + **acid**). In the first experiment you have, clearly:

$$\underbrace{(\textbf{calx} + \phi)}_{\textbf{metal}} + \textbf{acid} = \underbrace{(\textbf{calx} + \textbf{acid})}_{\textbf{salt}} + \underset{\textbf{inflammable air}}{\phi} .$$

in the second:

$$\textbf{calx} + \textbf{acid} = \underbrace{(\textbf{calx} + \textbf{acid})}_{\textbf{salt}}.\text{''}$$

This difficulty was serious: Lavoisier was unable to offer an explanation. The key was first supplied by the researches of Cavendish on the formation of water from inflammable air and dephlogisticated air.

SUMMARY OF CHAPTER III

The investigation of gases, different from air, made by Henry Cavendish in 1766, and Joseph Priestley (1774–86), was of great importance to chemistry. The theory of **combustion** and the **calcination of metals** due to Robert Hooke and John Mayow, in the seventeenth century, attributed these changes to the *absorption* of a gas from the atmosphere, which, since it is also fixed in nitre, was called **nitre air.** The **theory of phlogiston,** propounded in the next century by Becher and Stahl, explained the changes as due to the *escape* from the burning body of a subtle principle, called **phlogiston.**

The isolation of nitre air by Scheele (1772), and independently by Priestley (1774), enabled Lavoisier to overturn the theory of phlogiston, and to show that combustion consists in the union of the combustible substance with **oxygen** (nitre air), which is contained in the atmosphere to the extent of one-fifth of its volume.

EXERCISES ON CHAPTER III

1. Describe briefly the experiments of Boyle, Hooke, and Mayow on combustion, and state their conclusions.

2. Give an account of the theory of phlogiston, and show by an example how it was applied in the explanation of chemical changes. What experiments led to the downfall of the theory ?

3. Describe the work of Scheele which led to the isolation of *fire-air* (oxygen), and contrast the method used with Priestley's discovery of dephlogisticated air.

4. Describe the experiment of Lavoisier which proved that common air contains oxygen and nitrogen. What is meant by the "Anti-phlogistic theory"?

CHAPTER IV

THE COMPOSITION OF WATER

The work of Cavendish.—Priestley in 1781 observed that when a mixture of *dephlogisticated air* (oxygen) and *inflammable air* (hydrogen) is ignited it explodes violently. Warltire noticed that the sides of the bottle, after the explosion, are bedewed with moisture.

Expt. 33.*—Collect a mixture of 2 vols. of hydrogen and 1 vol. of oxygen in a strong soda-water bottle over water, draining out as much water as possible from the bottle. Insert a lump of fused calcium chloride in the bottle and cork it. When the moisture has been absorbed by the calcium chloride wrap the bottle in a strong towel, and ignite the gas by a taper. There is a loud explosion, and the inside of the bottle becomes filled with steam.

By firing the gases in a copper globe with the electric spark, Priestley thought he found that there was a slight loss of weight, which he put down to the escape of caloric (p. 36).

Cavendish in 1781 ignited a mixture of common air and inflammable air in a glass globe by means of the spark. He found that, with 423 vols. of inflammable air to 1000 vols. of common air, " almost all the inflammable air and about one-fifth part of the common air, lose their elasticity, and are condensed into the dew which lines the glass." There was no change in weight after explosion. He found the ratio of the combining volumes of hydrogen and oxygen to be 202 : 100.

To examine the nature of the dew, Cavendish performed an experiment similar to the following.

Expt. 34.—Burn a jet of hydrogen, dried by calcium chloride, under a glass retort, cooled by circulating cold water, as shown in Fig. 35.

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* This and similar experiments must be performed with adequate precautions to prevent injury in case the bottle should burst. The bottle is wrapped in a strong towel, with a short length of neck only projecting, and the whole placed in a strong tin can or iron mortar. A long taper is used.

Notice the collection of moisture on the outside of the retort. This runs down, and may be collected in a small dish. It will be found that this liquid is odourless, tasteless, boils at 100°, and leaves no residue on evaporation. It is **water.**

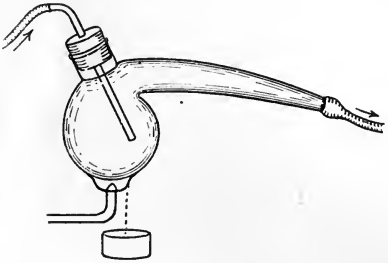

FIG. 35.—Formation of Water by Combustion of Hydrogen.

Cavendish now prepared a mixture of 195 vols. of dephlogisticated air and 370 vols. of inflammable air in a bell-jar over water. The end of a siphon tube, attached to the previously exhausted glass firing-globe or eudiometer (Fig. 36), was covered with a bit of wax and passed inside the jar. The wax was knocked off, and on opening the stopcock the globe was filled with the mixture. The cock was closed, and the mixture fired by a spark. The gas "lost its elasticity," and on opening the stopcock the globe was again filled with the gas, which took the place of that converted into liquid water by the explosion. This was repeated six times, and water was produced, which, however, was distinctly *acid.*

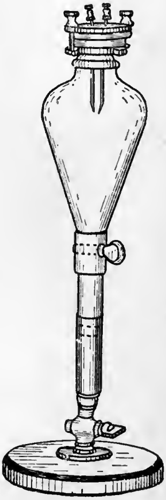

FIG. 36. Cavendish's Eudiometer.

Cavendish proved that the acidity was due to **nitric acid**. It was only formed when the oxygen was in excess, and was due to the combination with oxygen of nitrogen present in it as an impurity. By sparking air over water, the latter was found to contain nitric acid. Acid is not produced in the explosion of hydrogen with common air, because the flame is then not hot enough. If a slight excess of hydrogen is used with oxygen containing a little nitrogen, no acid is produced, since it is reduced, if formed, by the hydrogen.

On account of his attempts to find the cause of the acidity of the water, Cavendish delayed publication of his memoir until 1784. His conclusions were curious: "I think we must allow that dephlogisticated air is in reality nothing but dephlogisticated water; . . . and that inflammable air is either pure phlogiston, as Dr. Priestley and Mr. Kirwan suppose, or else water united to phlogiston . . . the second of these explanations seems much the most likely." He therefore represented the formation of water as follows :

$$\begin{array}{ll} \text{Inflammable air} & = \text{water} + \phi \\ \text{Dephlogisticated air} & = \underline{\text{water} - \phi} \\ & \quad \underline{2 \text{ water.}} \end{array}$$

Cavendish.

The ratio of the combining volumes of hydrogen and oxygen found in these experiments was 201 : 100.

Cavendish's choice of (water + ϕ) for inflammable air was based on the circumstance that it requires a red heat to start the combination of the two gases, whereas **nitric oxide** (*cf.* p. 578) combines at the ordinary temperature with dephlogisticated air, and in presence of moisture forms nitric acid. Nitric oxide, produced by the action of copper on nitric acid, was regarded as (nitric acid + ϕ), and it is not likely that dephlogisticated air should be able to separate ϕ from its combination with nitric acid but not able to unite with free ϕ (if this is inflammable air) under the same conditions. Hence inflammable air is probably not pure phlogiston, but phlogisticated water.

Cavendish therefore thought that *water pre-existed in the two gases, and its formation on explosion was simply due to a transfer of phlogiston.*

James Watt is usually credited with stating, in a letter published in 1784, that water *is composed* of the two gases, but Sir E. Thorpe (*Brit. Assoc. Rep.*, 1890) has given reasons for doubting this.

Lavoisier's explanation of Cavendish's experiments.—Lavoisier had been considerably puzzled by the product of the combustion of hydrogen in oxygen, which he thought must be an acid. In 1783 he resolved to make the experiment of burning hydrogen in oxygen on a larger scale, so that the product, whatever it was, should not escape his notice. In May or June of that year, however, Sir Charles Blagden, who was formerly Cavendish's assistant, visited Lavoisier, and told him of Cavendish's experiments. Lavoisier at once saw the importance of the result, and on June 24th, 1783, he repeated the experiments in the presence of Blagden. On the following day an account of them was sent to the French Academy of Sciences, and was published in the *Mémoires* which were **dated 1781**. Practically no mention is made of Cavendish, whose paper did not appear, for reasons just given, until **1784**. Lavoisier's claims to the discovery of the composition of water were, however, dismissed by his countryman Arago as pretentious. To Lavoisier, nevertheless, must be accorded the credit of having first clearly stated the results. In 1788 he says: "Water is nothing but oxygenated hydrogen, or the immediate product of the combustion of oxygen gas with hydrogen gas, deprived of the light and caloric which disengage during the combustion."

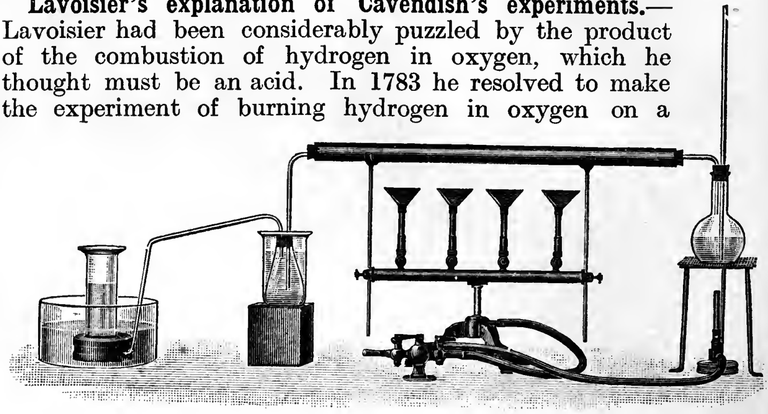

FIG. 37.—Decomposition of Steam by Red-hot Iron.

In 1784 Lavoisier and Meusnier decomposed water by passing its vapour over iron borings heated to redness in a gun-barrel. Hydrogen was liberated, and the iron converted into the same black oxide as is produced when iron wire burns in oxygen.

Expt. 35.—A piece of *weldless* iron pipe is loosely packed with iron turnings, and placed in a combustion furnace (Fig. 37). Rubber stoppers are fitted to the two ends of the pipe (which should project a fair distance from the furnace so as not to get too hot) and connected with a flask of water at one end, and an empty flask and gas delivery tube at the other, as shown. Heat the iron tube to redness and boil the water in the flask. Water collects in the empty flask, showing that the decomposition is not complete, but bubbles of gas are evolved from the delivery tube. Collect a jar of the gas, and show that it is hydrogen. After the experiment, examine the residue in the tube.

Expt. 36.—The decomposition of steam by magnesium may be shown by inserting a piece of burning magnesium ribbon into a large conical flask in which a little water is boiling vigorously. The metal burns brightly in the steam, and the hydrogen produced burns at the mouth of the flask; white magnesium oxide is left after the combustion.

Monge in 1783 exploded hydrogen and oxygen, drawn from two graduated jars, in a previously evacuated glass globe with firing wires (Fig. 38). No fewer than 370 successive explosions were made, producing four ounces of water, and the hydrogen and oxygen combined in the ratio of 1·95 : 1 by volume. The result is less accurate than that of Cavendish.

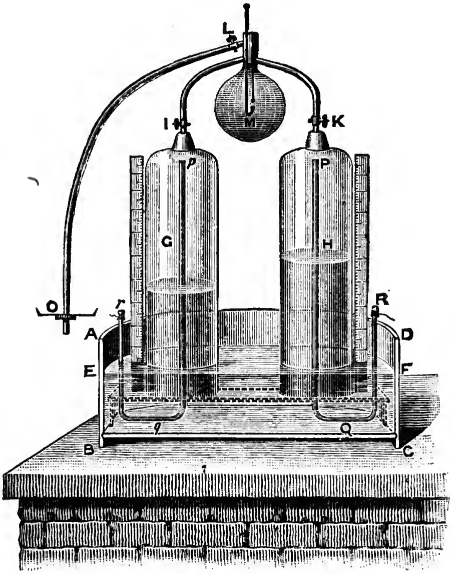

Fig. 38.—Monge's Experiment on the Combination of Hydrogen and Oxygen Gases.

The gases were collected through syphon-tubes, *pr*, PR, in the graduated cylinders, G and H; they passed through the stopcocks, I and K, to the globe, M, previously exhausted through the tap, L, leading to an air-pump at O.

Lavoisier was now able to explain the difficulty mentioned on p. 49, and so remove the last argument against the antiphlogistic theory. A metal, such as zinc, when it dissolves in dilute acid, decomposes the water, liberating hydrogen and combining with oxygen to form the calx (oxide), which then unites with the acid to form a salt. The origin of the inflammable gas was therefore cleared up. Lavoisier regarded the acid as an oxide; at present it is regarded as (oxide + water), so that the hydrogen really comes from the acid.

From 1785 the theory of phlogiston gradually disappeared. At the beginning of the nineteenth century practically every chemist, except Priestley and Cavendish (whose work had done so much to overturn it), had abandoned the theory, and the science of chemistry as we know it to-day had its origin in Lavoisier's writings. Its foundations had been laid by the investigations of Priestley, Cavendish, and Scheele, but it required the clear and original mind of the great French chemist to form these into a logical and harmonious system.

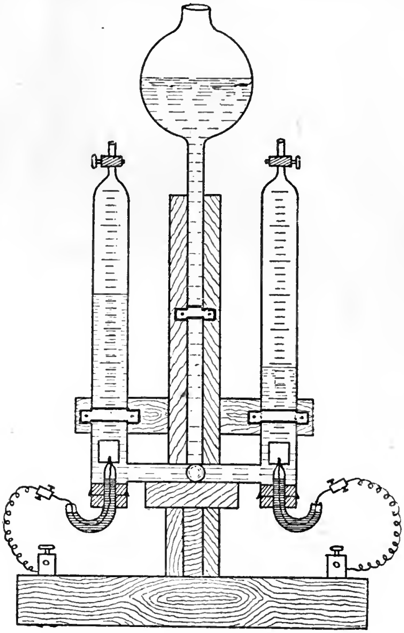

Fig. 39.—Electrolysis of Water.

The electrolysis of water.—In 1801 Nicholson and Carlisle, when experimenting with the newly-invented electric battery, discovered that if two gold wires connected with the copper and zinc poles of the battery are dipped into water, bubbles of oxygen and hydrogen, respectively, rise from these wires. If copper or iron wires are used, only hydrogen comes off; the oxygen is absorbed by the wire, producing an oxide. Cruickshank in 1802 collected the gases separately, and found that 2 vols. of hydrogen and 1 vol. of oxygen were liberated. This agrees with Cavendish's result of the synthesis of water. Davy in 1806 showed that if very pure water is electrolysed in a gold vessel, and the experiment carried out in a vacuous receiver, so that no impurities can enter from the air, or be dissolved from glass or other substances of ordinary vessels, then nothing but hydrogen and oxygen are produced. Thus **water is decomposed by the electric current into hydrogen and oxygen in the ratio of 2 to 1 by volume.**

EXPT. 37.—An apparatus for the decomposition of water by the current, or the **electrolysis of water,** is shown in Fig. 39. It is called a **voltameter** or **coulometer,** and consists of two graduated glass tubes, with stopcocks above, connected by a horizontal tube, carrying a funnel for filling the apparatus with dilute sulphuric acid. The **electrodes** for leading the current into and out of the liquid consist of pieces of platinum foil, welded to stout platinum wires sealed into bent glass tubes inserted through rubber corks (Fig. 40). These tubes are filled with mercury, copper wires dipping into which are connected with binding screws in the wooden stand. To these binding screws the wires from the source of current are attached.

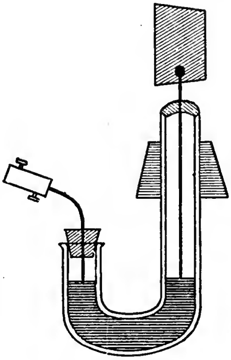

FIG. 40. — Details of Platinum Electrode.

Direct current may conveniently be taken from the supply mains at 110–220 volts, a lamp-resistance being inserted in the circuit. If no such current is available, four or six bichromate cells or accumulators in series will be found suitable.

Bubbles of gas rise from each electrode; that coming from the positive wire, although it appears more abundant because it is liberated in smaller bubbles, will be found to occupy very slightly less than half the volume of the other gas, and, if allowed to escape from the tap on to a glowing chip of wood, will rekindle the latter. This gas is **oxygen.** The other gas, evolved from the negative wire, when ignited by a taper, burns with a blue flame, and is **hydrogen.** Thus, **water is decomposed by electrolysis into 2 vols. of hydrogen + 1 vol. of oxygen.**

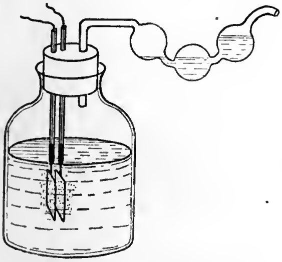

FIG. 41.—Preparation of Electrolytic Gas.

EXPT. 38.—**Electrolytic Gas.**—If two electrodes are placed in a bottle of dilute acid (Fig. 41), the hydrogen and oxygen gases come off mixed together in the form of **electrolytic gas.** This is washed from acid spray by a little water in the bulb tube, and collected over water in a stout soda-water bottle. This is wrapped in a towel, and the gas ignited with a taper (p. 51). A very violent detonation occurs (hence electrolytic gas is sometimes called **detonating gas**).

EXPT. 39.—A thin glass flask is filled with the mixture and inverted over a cork carrying two stout copper wires connected with a Ruhmkorff coil (Fig. 42). The flask is covered with a cage of stout fine-mesh iron wire gauze and a spark passed. There is a violent detonation, and the flask is shattered, a little finely-powdered glass escaping through the gauze in the form of white smoke.

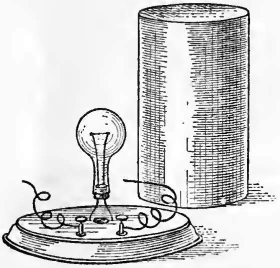

FIG. 42.—Explosion of Electrolytic Gas by an Electric Spark.

The Volumetric Composition of Water.

EXPT. 40.—Detonating gas is passed into a stout graduated glass tube, with sparking-wires above, filled with mercury, and inverted in a trough of that metal (Fig. 43). This tube is called a **eudiometer.** When a little gas has collected, the eudiometer is held down firmly on a pad of rubber moistened with mercuric chloride solution, beneath the mercury. On passing an electric spark, there is a flash of light in the tube, accompanied by a dull noise (not an explosion), and on raising the eudiometer, mercury rushes in and fills it, with the exception of a few drops of water which are seen floating on the surface of the metal.

A more convenient form of eudiometer is shown in Fig. 44. It consists of a strong glass **U**-tube filled with mercury, graduated, and provided with a stopcock and firing wires on one side; the other limb is a plain open tube, with a stopcock below for running off mercury. About 4 c.c. of electrolytic gas are introduced through the stopcock, mercury being run off from the lower stopcock. A large volume of mercury is now run out, so as to lower the pressure of the gas, the thumb is pressed firmly over the open end of the tube, and the gas fired by a spark.

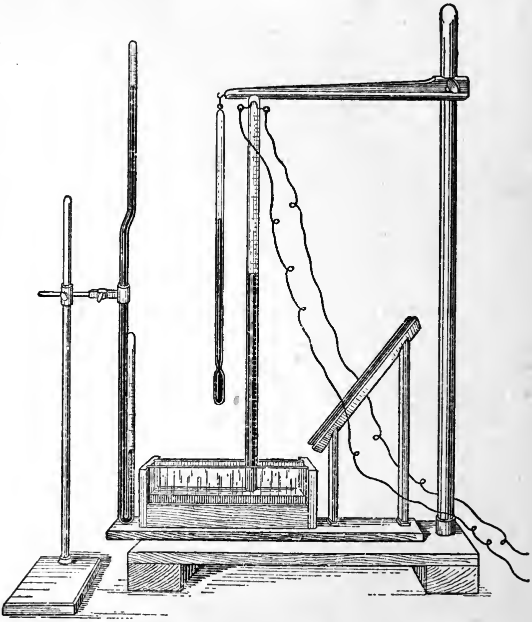

FIG. 43.—Eudiometer for Explosion of Gases by an Electric Spark.

Expt. 41.—By using a **U**-shaped eudiometer, the graduated limb of which is surrounded by a glass jacket through which the vapour of boiling amyl alcohol (131–132°) is passed, the water produced by the explosion is kept in the form of vapour (Fig. 45). Thirty c.c. of electrolytic gas are introduced, measured at the temperature of the jacket, with the mercury levels adjusted to equality on both sides by lowering the mercury reservoir. The open end of the **U**-tube is firmly closed by the thumb, and a spark passed from the coil. There is a flash of light, and an immediate contraction when the thumb is removed. By running mercury into the open limb until the levels are again equal, it will be seen that the residual steam occupies 20 c.c. The 30 c.c. of electrolytic gas contained, as we know, 20 c.c. of hydrogen and 10 c.c. of oxygen, hence :

2 vols. of hydrogen + 1 vol. of oxygen = 2 vols. of steam.

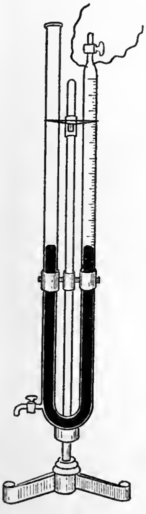

Fig. 44.
U-shaped
Eudiometer.

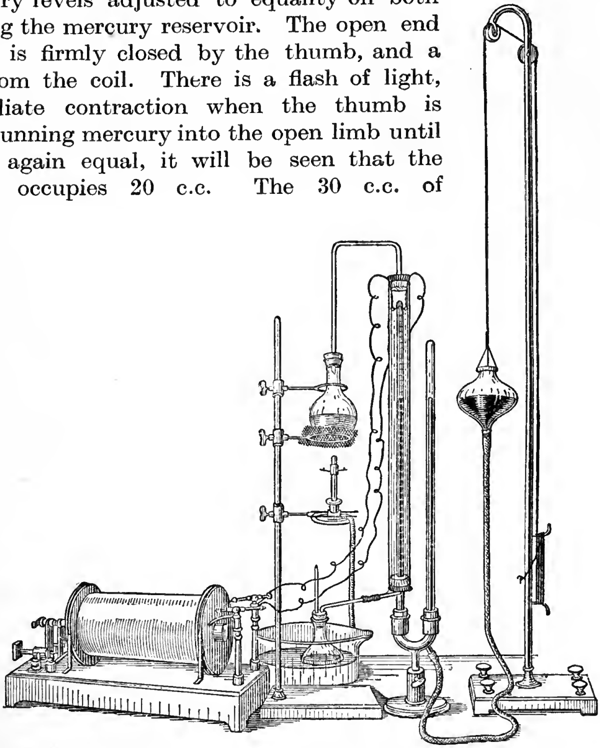

Fig. 45.—Volumetric Composition of Steam.

The accuracy attained in these experiments is not sufficient to give the exact figure for the combining volumes of the gases. Cavendish's result, giving the ratio of the volumes of hydrogen and oxygen uniting to form water as 201 : 100, is very near the ratio 2 : 1, which was accepted until 1888. The more exact experiments made since that date have shown that the ratio is probably very nearly 200·3 : 100, but a description of these experiments is deferred until Chapter XII.

The composition of water by weight.—Since it is difficult to weigh with accuracy large volumes of hydrogen and oxygen, it is only comparatively recently that the composition of water by direct synthesis from its elements has been attempted. Formerly an indirect method was used. A stream of hydrogen, which is not weighed, is passed over weighed copper oxide (prepared by heating copper turnings in air) heated to dull redness. The oxide is reduced by the hydrogen to metallic copper, the oxygen of the oxide uniting with the hydrogen to form water, which is collected and weighed. From these results we find :

Loss of weight of copper oxide = weight of oxygen = o.
Weight of water − weight of oxygen = weight of hydrogen = h.
∴ Ratio of combining weights = o/h.

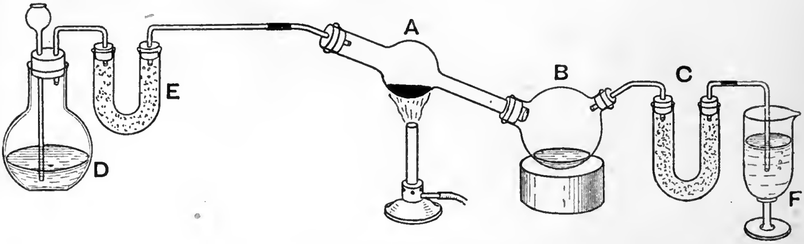

Fig. 46.—Gravimetric Composition of Water.

It will be seen that the weight of hydrogen is obtained by difference, so that the synthesis is not complete.

This method was applied by Berzelius and Dulong in 1819, who obtained the ratio : **oxygen** : **hydrogen** : : 8·01 : 1, approximately.

Expt. 42.—About 20 gm. of black oxide of copper, previously heated to redness in a crucible and cooled in a desiccator over calcium chloride to remove moisture, are introduced into a hard glass bulb-tube, *A* (Fig. 46), which is then weighed. The tube is connected by a rubber or ground glass joint to a small receiver, *B*, attached by a rubber stopper to a **U**-tube, *C*, filled with granular calcium chloride, a substance which readily absorbs water vapour (p. 203). The receiver, *B*, and tube, *C*, are weighed together.

A current of hydrogen, generated from pure zinc and dilute sulphuric acid in the flask, *D*, and dried by the calcium chloride tube, *E*, is then passed through the apparatus until all the air is expelled. The gas bubbles out through sulphuric acid in the glass, *F*. The copper oxide is then heated by a Bunsen flame. Drops of moisture at once condense in the lower part of *A* and in the receiver, *B*, and the black oxide of copper is reduced to red metallic copper. *B* is kept cool in a vessel of cold water, and as the experiment proceeds and *A* becomes warm, all the water is driven over into *B* and *C*. The apparatus is allowed to cool, with hydrogen still passing. The tube *A*, and *B* and *C*, are again weighed.

The gain in weight of *B* and *C* gives the weight of water formed. The loss in weight of *A* gives the weight of oxygen given up by the copper oxide to the hydrogen to produce this water. The difference between the weight of the water and the loss of weight of the copper oxide gives the weight of hydrogen.

In 1842 Dumas carried out this experiment with all the accuracy possible at the time. Hydrogen was generated from zinc and dilute sulphuric acid, and was purified by passing through a train of seven **U**-tubes containing: (1) lead nitrate solution to remove sulphuretted hydrogen, (2) silver nitrate solution to remove arseniuretted hydrogen, (3) three tubes of caustic potash to remove acid vapours, (4) two tubes of sulphuric acid cooled in ice, or phosphorus pentoxide, to dry the gas. The reagents were distributed on pumice or broken glass to expose a large surface.

The copper oxide was contained in a large hard glass bulb with a long neck. This was weighed after evacuation to remove the air. The air was displaced from the apparatus by hydrogen, and the bulb heated by a large spirit lamp for ten to twelve hours. The water produced was collected in a smaller bulb, in the neck of which calcium chloride was placed, followed by a series of four drying tubes containing sulphuric acid on pumice, or phosphorus pentoxide. The last tube communicated with a vessel of sulphuric acid, through which the residual hydrogen escaped. In all the experiments the weight of the last absorption tube was constant. The whole apparatus is shown in Fig. 47.

The copper was allowed to cool in the bulb in a stream of hydrogen, the hydrogen was displaced by air in the whole apparatus, and the bulb then exhausted and weighed. The absorption system was also weighed.

A mean of nineteen experiments gave the following result:

	Percentage by weight.	Combining ratio by weight.
Oxygen	88·864	7·98
Hydrogen	11·136	1·00
	100·000	8·98

This ratio was accepted without question for nearly half a century. Dumas himself, however, had pointed out two sources of error in the method :

(1) Air dissolved in the sulphuric acid passed on with the hydrogen,

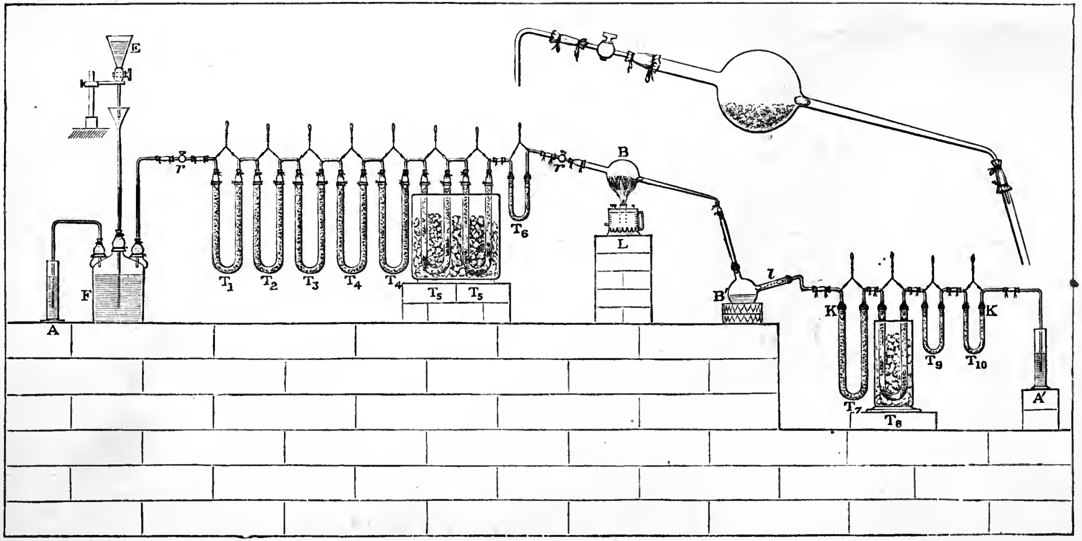

FIG. 47.—DUMAS' APPARATUS FOR DETERMINING THE COMPOSITION OF WATER.

The copper oxide bulb, B, is shown above on a larger scale. The apparatus consisted of the following parts:—F, a Woulfe's bottle for the generation of hydrogen; E, a tap-funnel containing sulphuric acid; A, a mercury safety-valve; T_1, a tube containing lead nitrate spread on broken glass; T_2, a tube containing glass moistened with silver sulphate; T_3, a tube containing (*a*) pumice soaked in potash solution, (*b*) solid potash; T_4, T_4, tubes containing pieces of potash; T_5, T_5, tubes containing phosphorus pentoxide (or sometimes sulphuric acid) spread over pumice, cooled in a freezing mixture; T_6, a "témoin" or guard-tube containing phosphorus pentoxide and pumice; B, the bulb containing copper oxide, with stopcock and pointed tube delivering into the receiver, B′, for collecting the water, with fragments of calcium chloride at *l*; L, a large spirit-lamp for heating the bulb; T_7, a tube of solid potash; T_8, a tube of phosphorus pentoxide (or sulphuric acid) on pumice, cooled in a freezing mixture; T_9, a témoin tube of phosphorus pentoxide; T_{10}, a guard-tube of phosphorus pentoxide (not weighed) to exclude moisture; A′, escape-valve for excess of hydrogen, containing sulphuric acid.

and the oxygen of this air combined with hydrogen in the copper oxide bulb ;

(2) The reduced copper retained hydrogen when cooled in that gas. Both errors tended to reduce the loss of weight of the bulb, so that the proportion of oxygen found would be too small.

In 1890 Dittmar and Henderson found an additional error in Dumas' method. In drying hydrogen with sulphuric acid, sulphur dioxide is formed. When this is passed with hydrogen over heated copper, the oxygen of the sulphur dioxide combines with the hydrogen to form water, whilst the sulphur remains in combination with the copper as sulphide. The loss in weight of the copper oxide bulb is therefore seriously too small. By using hydrogen dried with caustic potash and phosphorus pentoxide, however, these experimenters found the still lower ratio *oxygen* : *hydrogen* : : 7·93 : 1.

Keiser in 1888 introduced the method of weighing the hydrogen absorbed in palladium (p. 71) ; he weighed the water formed on pumping the gas over heated copper oxide, which was not weighed. Oxygen was found by difference and the ratio was found to be 7·935—7·975 to 1. Noyes in 1890 burnt hydrogen in a copper oxide bulb and condenser made in one piece, the increase of which gave the weight of hydrogen. The water was removed and its weight found. The loss of weight of the apparatus gave the weight of oxygen. Thus a complete synthesis was effected, and the result was the ratio 7·947 : 1.

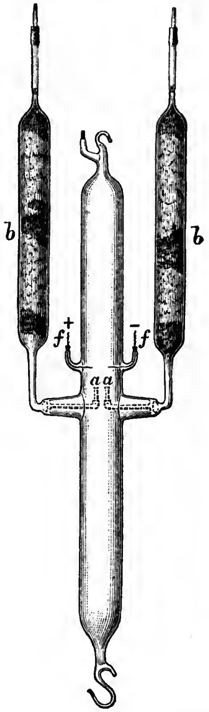

FIG. 48.—MORLEY'S COMBUSTION-TUBE.

The gases passed through phosphorus pentoxide drying tubes, *b*, *b*, to the jets, *a*, *a*, where they were ignited by electric sparks between *f* and *f*.

The most exact experiments on the composition of water by weight are those of E. W. Morley (1895). Purified oxygen and hydrogen gases were weighed in large glass globes ; in the later experiments the hydrogen was weighed in a bulb of palladium. The gases were then burnt at platinum jets in a previously evacuated sealed glass vessel (Fig. 48), immersed in cold water, the gases being ignited by an electric spark between the wires shown. The water was then frozen, and the residual gas pumped out through a tube containing phosphorus pentoxide (to keep back water vapour), and analysed.

A typical experiment furnished the following data :

Weight of hydrogen introduced into apparatus = 3·8223 gm.
,, residual hydrogen = 0·0012 ,,
∴ ,, hydrogen burnt = 3·8211 ,,
,, oxygen introduced into apparatus = 30·3775 ,,
,, residual oxygen = 0·0346 ,,
∴ ,, oxygen burnt = 30·3429 ,,
Sum of weights of hydrogen and oxygen burnt = 34·1640 ,,
Weight of water produced = 34·1559 ,,
∴ Loss in weight due to experimental error = 0·0081 ,,

Ratio of weights of oxygen and hydrogen combining to form water = 7·941 : 1.

As a final result, the mean of twelve experiments in which 400 gm. of water were produced, Morley obtained the ratios :

Oxygen : hydrogen :: 7·9396 : 1
Water : hydrogen :: 8·9392 : 1.

By his other series of experiments on the densities and combining volumes of the two gases (pp. 72, 213), Morley found the ratio :

Oxygen : hydrogen :: 7·9395 : 1.

These researches are probably the most exact chemical investigations ever executed.

SUMMARY OF CHAPTER IV

The formation of **water** on the explosion of a mixture of hydrogen and air, or oxygen, was noticed by Priestley (1781). More exact experiments of Cavendish (1781–1784) established the fact that almost exactly 2 vols. of hydrogen and 1 vol. of oxygen combine to form water, but the clear statement that water is composed of these substances is due to Lavoisier (1785). Nicholson and Carlisle (1801), and Cruickshank (1802), found that water is decomposed into its elements by an electric current (**electrolysis**), the hydrogen appearing at the negative pole and the oxygen at the positive. No other substances are produced from pure water (Davy, 1806).

The **volumetric composition of water** has been determined by exploding measured volumes of the gases, and measuring the residual gas. Scott (1887–93) found *oxygen/hydrogen* = 1 : 2·00285 ; Burt and Edgar, in a very careful research (1915), found the ratio 1 : 2·00288 (p. 213).

The **gravimetric composition of water** was determined by : (1) passing hydrogen over heated copper oxide ; (2) burning weighed quantities of hydrogen and oxygen, and weighing the water. Dumas (1842), by method (1), found : *hydrogen/oxygen* = 1 : 7·98 ; Dittmar and Henderson (1890) found errors in Dumas' method, and obtained 1 : 7·93. Cooke and Richards (1887) found 1 : 7·934, Keiser (1888) 1 : 7·93. By method (2) Rayleigh (1889) found 1 : 7·945, and Morley (1895) 1 : 7·9396.

EXERCISES ON CHAPTER IV

1. Give a short account of the work leading to the discovery of the composition of water, stating the share of each investigator in the elucidation of the problem.

2 How would you proceed to illustrate by experiment the composition of water by weight and by volume ?

3. Describe any investigation in which the composition of water has been accurately determined.

4. 21·40 gm. of lead oxide are heated in a current of hydrogen, and, after reduction, the weight was 19·46 gm. What weight of water has been formed ?

5. Describe experiments designed to produce (*a*) detonating gas, (*b*) oxygen and hydrogen gases separately, from water. How may the relative volumes of detonating gas and the steam produced from it by explosion be compared, and what is the result ?

CHAPTER V

THE PHYSICAL PROPERTIES OF GASES AND VAPOURS

Compression of gases : Boyle's law.—The discussion of **gaseous pressure,** and that of the effects of changes of volume and temperature on the pressure of a gas, belong to physics. A brief summary of the results, presented in such a form as to be immediately applicable to chemical problems, may, however, be given here.

Effect of pressure on volume.—**Boyle's law** (1662) : **When the temperature is maintained constant, the volume of a given mass of gas is inversely proportional to the pressure :**

$$pv = \text{constant} = C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The **density** of a gas is the mass per unit volume, m/v, hence **the density is proportional to the pressure.** If we call the mass of gas in grams which occupies 1 c.c. its **concentration,** then at constant temperature **the pressure is proportional to the concentration.**

Boyle's law is not exact ; all gases show marked deviations from it at high pressures. At moderate pressures all common gases except hydrogen are more compressible than an **ideal gas** which obeys Boyle's law. Hydrogen is slightly less compressible, and the same behaviour is shown by all gases at very high pressures (Amagat).

Table of Relative Volumes occupied by various gases when 1 vol. at the given pressure is reduced to atmospheric pressure. Temperature 16°.

	50 atm.	100 atm.	120 atm.	150 atm.	200 atm.
Ideal gas	50	100	120	150	200
Hydrogen	48·5	93·6	111·3	136·3	176·4
Nitrogen	50·5	100·6	120·0	147·6	190·8
Air	50·9	101·8	121·9	150·3	194·8
Oxygen	—	105·2	—	—	212·6
Do. at 0°	52·3	107·9	128·6	161·9	218·8
Carbon dioxide	69·0	477*	485*	498*	515*

* Liquefied at pressures greater than 90 atm.

At very low pressures (0·01–1·5 mm. Hg) no deviation from Boyle's law can be detected (Rayleigh, 1901–2). Boyle's law appears to be exact under such conditions, and the gases behave like the ideal gas.

Effect of temperature : Charles's law.—Dalton in 1801 observed that gases expanded by equal increments of their volumes for equal rises of temperature; his results were published in 1802. In the same year Gay-Lussac published a memoir, in which he stated that Charles, in 1787, had found that gases expand equally between 0° and 80°, but did not measure the expansion. Gay-Lussac, from his own experiments, derived the law in question, which differs from Dalton's in the reduction of the initial volume to 0°. It is known as **Charles's law : at constant pressure all gases expand by 1/273 of their volume at 0° C. for a rise of temperature of 1°.**

Let v_0 = volume at 0°, v_t = volume at t°, under the same pressure, then $v_t = v_0\left(1 + \frac{t}{273}\right)$, or $v_t/v_0 = (273 + t)/273$. If v_1, v_2 are the volumes corresponding to two temperatures t_1°, t_2°,

$$v_2/v_1 = (273 + t_2)/(273 + t_1).$$

The value $(t_1 + 273)$ is called the **absolute temperature,** T_1, corresponding to t_1; hence, **the volumes are proportional to the absolute temperatures** (p const.): $v_2/v_1 = T_2/T_1$. If we put $t = -273$, then $T = 0$, and by substitution in the equation we find that $v = 0$. The temperature $-273°$ is called the **zero of absolute temperature,** or the **absolute zero.** It can be proved by thermodynamics that it is impossible to cool a body below the absolute zero. By the rapid evaporation of liquid helium in a vacuum, Kamerlingh Onnes obtained a temperature of $-271·5°$, or only 1·5° above the absolute zero.

If the volume of a given mass of gas is kept constant, **the pressure increase for 1° is 1/273 of the pressure at 0°.** This is readily proved from Boyle's and Charles's laws. Thus $p_2/p_1 = T_2/T_1$.

If volume and temperature change together, it is readily shown in the same way (*cf.* Duncan and Starling's "Text-book of Physics" (Macmillan), p. 406) that : $p_1v_1/T_1 = p_2v_2/T_2$; or, generally, $pv/T =$ *constant,* for a given mass of gas.

Charles's law is not strictly true; the **coefficients of expansion** of gases differ slightly among themselves, and from 1/273, and the change of pressure at constant volume is slightly different from the change of volume at constant pressure, for the same rise of temperature. At very low pressures, however, these magnitudes approach equality, the limiting value being 1/273·09. The exact value of the absolute temperature of melting ice is therefore 273·09°. For the **ideal gas** the coefficient of expansion is 1/273·09 = 0·0036618.

Example 1. **Boyle's law.**—A volume of gas occupies 224 c.c. when under a pressure of 755 mm. What will be its volume under a pressure of 760 mm., if the temperature remains constant ?

The volume is inversely proportional to the pressure :

$$\therefore \quad v_1 : v_2 :: p_2 : p_1,$$

$$\therefore \quad 224 : v_2 :: 760 : 755,$$

$$\therefore \quad v_2 = 224 \times \frac{755}{760} = \mathbf{222{\cdot}5\ c.c.}$$

Alternative method :—**pv = constant** $\therefore p_1 v_1 = p_2 v_2$,

$$\therefore \quad v_2 = v_1 \cdot \frac{p_1}{p_2} = 224 \times \frac{755}{760} = \mathbf{222{\cdot}5\ c.c.}$$

Example 2. **Charles's law.**—450 c.c. of gas are collected at a temperature of 16°. What will be the volume at 0° if the pressure remains unchanged ?

The volume is proportional to the absolute temperature :

$$t_1^\circ \text{ C.} = 273^\circ + t_1^\circ \text{ abs.} = T_1^\circ \text{ abs.} = 273^\circ + 16^\circ = 289^\circ \text{ abs.}$$

$$t_2^\circ \text{ C.} = 273^\circ + t_2^\circ \text{ abs.} = T_2^\circ \text{ abs.} = 273^\circ \text{ abs.}$$

$$v_1 : v_2 :: T_1 : T_2 \quad \therefore \quad v_2 = v_1 \times \frac{T_2}{T_1} = 450 \times \frac{273}{289} = \mathbf{425{\cdot}1\ c.c.}$$

Example 3. **Combined gas law.**—A quantity of hydrogen at 15° and 750 mm. pressure occupies 4·5 litres : what will be its volume at 0° and 760 mm. ?

$$v_2 = v_1 \times \frac{p_1}{p_2} \times \frac{T_2}{T_1} = 4{\cdot}5 \times \frac{750}{760} \times \frac{273}{288} = \mathbf{4{\cdot}209\ litres.}$$

The density of a gas.—The **density of a gas,** or **vapour,** is expressed in two ways :—

(1) The **normal density,** or simply **density,** of a gas or vapour is the weight in grams of 1 litre (or 1000·027 c.c.) of the substance, measured at a temperature of 0°, and under a pressure of 760 mm. of mercury, the weights being reduced to sea-level, and latitude 45°.

One **litre** is defined as the volume occupied by 1 kilogram of water, at 4°, weighed in vacuum at sea-level, and latitude 45°. One **cubic centimetre** is the capacity of a centimetre cube, the centimetre being one-hundredth of the length of the standard metre. Owing to a slight inconsistency in the Metric System, the volume of 1 gram of water at 4° is not 1 c.c., but 1·000027 c.c. Since weight is slightly variable with the position on the earth, it is referred to standard conditions, sea-level and lat. 45°.

(2) The **relative density** of a gas, or vapour, is the weight of any volume of the substance divided by the weight of an equal volume of pure hydrogen, measured and weighed under the same conditions.

Hydrogen is chosen as the standard substance because it is the lightest gas known.

Standard temperature and pressure (or **normal** temperature and pressure), denoted by S.T.P. (or N.T.P.), are 0° C. (273·09° absolute), and the pressure of a column of 760 mm. of mercury at 0° at sea-level, and at latitude 45°. On account of slight deviations of gases from the laws of Boyle and Charles, the relative density in accurate work is determined with both gases actually at S.T.P., so that no corrections by the gas laws are necessary. With vapours this is, of course, impossible, but, on account of the very large deviations of vapours from the gas laws, an approximate value of the relative density is all that is in this case determined and required.

Determination of gas densities.—The density of a gas is determined by weighing an evacuated globe, filling it with the gas, and reweighing. The volume of the globe is determined by filling it with water and reweighing.

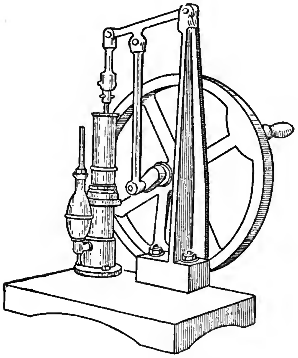

FIG. 49.—Air-pump.

EXPT. 43.—Fit a 1 litre round-bottomed flask with a rubber stopper and glass stopcock (Fig. 20). Evacuate the flask by a good Fleuss or Geryk oil-pump (Fig. 49), or a metal water-pump with a calcium chloride tube attached to prevent diffusion of moisture into the flask. Weigh by suspending on one arm of a large sensitive balance. Connect the flask with a gas-holder of carbon dioxide, interposing a calcium chloride tube. Open the stopcocks on the gas-holder, and slightly open the stopcock on the evacuated flask so as to allow the gas to stream *slowly* into it. When the pressure is equalised, run out water from the gas-holder by the lower tap until the level of water in the funnel tube is the same as that inside the gas-holder, and close the stopcock on the flask. Reweigh the latter. Now fill the flask with water to the level of the cork and weigh on a rough balance to find the volume of the flask (assume 1 gm. = 1 c.c.). Read the barometer and the temperature of the water in the gas-holder. Calculate the density of carbon dioxide at S.T.P.

If the globe is weighed first vacuous, then full of the gas, and finally filled with hydrogen under the same conditions, the **relative density** is given by:

$$\frac{\text{weight of gas filling globe}}{\text{weight of hydrogen filling globe.}}$$

If the weighings are carried out under different conditions, the relative density is the ratio : $\frac{\text{density of gas (at S.T.P.)}}{\text{density of hydrogen (at S.T.P.)}}$.

EXAMPLE 1.—Weight of evacuated flask =148·563gm.
,, ,, flask filled with carbon dioxide =150·382 ,,
,, ,, ,, ,, ,, water = 1128·6 ,,

Temperature of gas = 15° ; pressure (barometer) = 758 mm.

Volume of flask = 1128·6 − 148·6 = 980 c.c. This volume is occupied by the carbon dioxide at 15° and 758 mm. pressure,

∴ volume of carbon dioxide at S.T.P.

$$= 980 \times \frac{758}{760} \times \frac{273}{288} = 926{\cdot}6 \text{ c.c.}$$

Weight of carbon dioxide = 150·382 − 148·563 = 1·819 gm.,

∴ **density** = weight of 1 litre (1000 c.c. approximately)

$$= \frac{1{\cdot}819 \times 1000}{926{\cdot}6} = \mathbf{1{\cdot}963}\ \frac{\text{gm.}}{\text{lit.}}$$

EXAMPLE 2.—Weight of above flask filled with hydrogen at 14° and 759 mm. pressure = 148·646 gm.

Volume of hydrogen at S.T.P. $= 980 \times \frac{759}{760} \times \frac{273}{287} = 930{\cdot}9$ c.c.

Weight of hydrogen = 148·646 − 148·563 = 0·083 gm.

∴ density of hydrogen $= \frac{0{\cdot}083 \times 1000}{930{\cdot}9} = 0{\cdot}089 \frac{\text{gm.}}{\text{litre.}}$

Relative density of carbon dioxide $= \frac{\text{density of carbon dioxide}}{\text{density of hydrogen}}$

$$= \frac{1{\cdot}963}{0{\cdot}089} = \mathbf{22{\cdot}05.}$$

The true weight (in vacuum) of the globe is the apparent weight in air *plus* the weight of air displaced by the globe : this latter value depends on the temperature, pressure, and degree of moisture of the air, and as these may be different during the separate weighings, corrections of all weights to vacuum will be necessary in accurate work. Also, the surface of the globe always carries a film of moisture condensed upon it from the atmosphere (*cf*. p. 23), which will vary with the moistness of the air. To eliminate these difficulties as far as possible Regnault introduced the use of **compensating globes.** The density globe was counterpoised on the balance by hanging on the other arm another globe of as nearly as possible identical weight and volume (Fig. 50), so that all variations of atmospheric conditions affected both globes equally, and the corrections were thus eliminated. The small adjustments of weight necessary, corresponding with the weights of the gases themselves, were made with ordinary metal weights, which are corrected to vacuum in calibration, and in any case have a negligible displacement.

A correction which remains to be made when this method is used was pointed out by Rayleigh (1888), viz., that due to the **shrinkage** of the globe on evacuation. This results in the globe displacing a little less air when it is evacuated than when it is full of gas, or than the compensating globe. The amount of shrinkage is found by pumping out the globe in a closed vessel filled with water, and observing the fall of level of the latter in a communicating graduated tube. With a globe of 2000 c.c. capacity the correction to be applied was 0·0006 gm. on the weight of hydrogen filling the globe, and Regnault's value of 0·08968 for the normal density of hydrogen had to be raised to 0·08988.

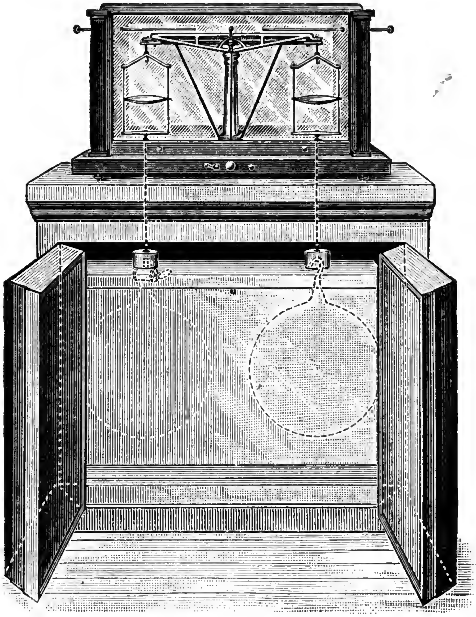

FIG. 50.—Determination of the Density of a Gas.

This method has been used by E. W. Morley (1896) in a very careful determination of the normal densities of hydrogen and oxygen, which are of fundamental importance in chemistry (p. 122). Very pure hydrogen gas was absorbed in a glass tube containing metallic palladium, which is capable of taking up considerable amounts of hydrogen, but not of gaseous impurities, so that the latter may be removed by pumping out the tube. On heating the palladium to dull redness, pure hydrogen is evolved from the metal, and the loss in weight of the tube gives the weight of gas. The hydrogen was received in three large evacuated glass globes, immersed in ice, the total volume of the globes being accurately known. The rise in pressure in the globes was then determined by a mercury manometer. One result is given below.

Volume of the three globes	43·2574 litres
,, ,, ,, gas space in manometer	0·0550 litre
,, ,, ,, connecting tubes	0·0365 ,,
Total volume of gas	43·3489 litres

Temperature 0°. Pressure 725·40 mm. Loss of weight of palladium bulb = weight of hydrogen = 3·7164 gm.

Correction to reduce weighings to sea-level and latitude 45°, and length of cathetometer to 0° = 1·00044,

∴ normal density of hydrogen

$$= \frac{3\cdot7164}{43\cdot3489} \times \frac{760}{725\cdot4} \times 1\cdot00044 = \mathbf{0\cdot089861\ gm./litre.}$$

As a mean of all his results, Morley found:

Normal density of hydrogen = 0·089873 ± 0·0000027 gm. per litre;
Normal density of oxygen = 1·42900 ± 0·000034 gm. per litre.

In comparing the first figure with the corrected result of Regnault, Morley's weighings must be reduced to the latitude of Paris. His value then becomes **0·089901**, differing from Regnault's, 0·08988, by less than 1 in 4000.

The following table gives the most recent values of **normal densities of gases,** determined with great exactness:

Air	1·2928	Nitrous oxide	1·9777	Hydrogen chloride	1·6398
Oxygen	1·42906	Nitric oxide	1·3402	Sulphur dioxide	2·9266
Hydrogen	0·08987	Ammonia	0·7708	Helium	0·1782
Nitrogen	1·2507	Carbon monoxide	1·2504	Neon	0·9002
Argon	1·7809	Carbon dioxide	1·9768	Methane	0·7168

The relative density of air is 1·2928 ÷ 0·08987 = 14·44. Formerly, densities of gases were referred to **air** = 1 instead of to **hydrogen** = 1; these values may be converted to the modern units by multiplication by 14·44. The composition, and therefore the density, of air vary slightly in different localities, hence the use of this gas as an accurate standard of relative density is strongly to be deprecated (p. 536).

The law of partial pressures.—If two or more gases, which do not react chemically, are mixed together in a closed vessel, **the pressure exerted by the mixture of gases is the sum of the pressures which each gas alone would exert if separately confined in the whole**

volume occupied by the mixture. (The temperature is assumed to be maintained constant throughout.) The pressures exerted by the separate gases are called their **partial pressures,** and the above statement is called the **law of partial pressures.** (Dalton, 1801.)

EXPT. 44.—Connect two globes, A and B (Fig. 51), of capacities about 2 and $\frac{1}{2}$ litres, respectively, with each other and a manometer as shown. Close the stopcocks T_2 and T_3 and partially evacuate A through the cock T_4. Close T_4 and establish connection with the manometer by opening T_3. Read the difference in mercury levels, and subtract from the reading of the barometer to find the pressure of the gas. Let the pressure in A be p_A mm. In the same way, reduce the pressure in B to p_B mm. Close T_3 and open T_1 and T_2. When the two quantities of air have mixed, and the temperature has regained the initial value, open T_3 and read the final pressure, p. Total volume $= v_A + v_B$, $\therefore$ partial pressures of the air in A and B, respectively, are $p_A \cdot \frac{v_A}{v_A + v_B}$ and $p_B \cdot \frac{v_B}{v_A + v_B}$, these, by Boyle's law, being the pressures the separate quantities of air would exert if each occupied the whole volume $v_A + v_B$. The sum of the partial pressures is $\frac{p_A v_A + p_B v_B}{v_A + v_B}$, and this will be found to be very nearly equal to p.

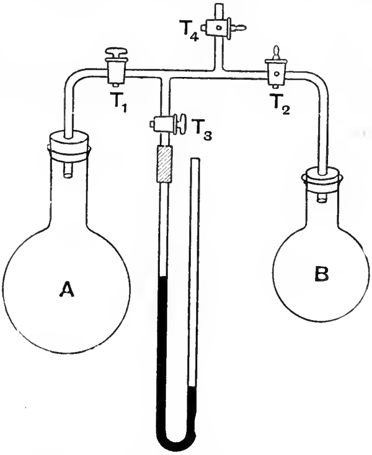

FIG. 51.—Experiment on the Law of Partial Pressures.

In one experiment the following results were found :—
Volume of large flask $= v_A = 2210$ c.c.
Volume of small flask $= v_B = 600$ c.c.
Pressure of gas in large flask $= 76 - 20$ cm. $= 56$ cm. mercury $= p_A$.
Pressure of gas in small flask $= 76$ cm. of mercury $= p_B$.

Partial pressure of first gas in mixture $= 56 \times \frac{2210}{2810} = 44$ cm.

Partial pressure of second gas in mixture $= 76 \times \frac{600}{2810} = 16{\cdot}2$ cm.

Observed total pressure after mixing $= 76 - 16 =$ **60 cm.**
Sum of partial pressures $= 44 + 16{\cdot}2 =$ **60·2 cm.**
(Air was used in both flasks.)

The law of partial pressures is not strictly exact; all real gases show slight deviations from it. Leduc has shown that the law given below is more exactly followed than the law of partial pressures: **the volume occupied by a mixture of gases is equal to the sum of the volumes which the component gases would occupy at the same temperature, and under the same pressure, as the mixture.** This has been verified with mixtures of hydrogen and nitrogen up to 200 atm. pressure.

EXAMPLE 1.—Two vessels, of capacities 500 c.c. and 2000 c.c., containing hydrogen and oxygen, respectively, under pressures of 750 mm. and 10 mm., are put in communication. What will be the final pressure of the mixture of gases?

Total volume $= v_A + v_B = 500$ c.c. $+ 2000$ c.c.

$\therefore$ partial pressure of hydrogen

$$= p_A \times \frac{v_A}{v_A + v_B} = 750 \times \frac{500}{2500} = 150 \text{ mm.},$$

and partial pressure of oxygen

$$= p_B \times \frac{v_B}{v_A + v_B} = 10 \times \frac{2000}{2500} = 8 \text{ mm.}$$

Total pressure = sum of partial pressures $= 150 + 8 =$ **158 mm.**

Alternative method: sum of partial pressures $= \dfrac{p_A v_A + p_B v_B}{v_A + v_B}$

$$= \frac{(750 \times 500) + (10 \times 2000)}{2000 + 500} = 158 \text{ mm.}$$

EXAMPLE 2.—154 c.c. of nitrogen, at 750 mm. pressure, are mixed with 50 c.c. of hydrogen, at 550 mm. pressure, in a vacuous globe of capacity 2000 c.c. What is the partial pressure of hydrogen in the mixture, and the total pressure?

nitrogen

Partial pressure of hydrogen $= 750 \times \dfrac{154}{2000} =$ **57·75 mm.**, independently of the presence of the other gas in the vessel.

Partial pressure of nitrogen in mixture $= 550 \times \dfrac{50}{2000} = 13{\cdot}75$ mm.

$\therefore$ Total pressure = sum of partial pressures $= 57{\cdot}75 + 15{\cdot}75 =$ **73·5 mm.**

Vapour pressure.—Liquids when admitted to vacuous spaces **evaporate,** or give off vapour, until the latter attains a definite pressure, which depends only on the temperature. The vapour is then said to be **saturated.** Dalton's law of partial pressures shows that the pressure of the vapour of a liquid in a closed vessel filled with an indifferent gas will also be the same as if the space were initially vacuous. If insufficient liquid be present to saturate the space, the vapour is said to be **unsaturated.**

EXPT. 45.—Fill two tubes about 78 cm. long, sealed at one end, and carefully cleaned and dried, with dry mercury, and invert in two small dishes containing mercury. The level of the mercury sinks in each tube, leaving a vacuous space above. Measure the level of mercury in each tube above the surface in the trough.

By means of small pipettes (Fig. 52) introduce a few drops of water into one tube, and a few drops of ether into the other. Notice the depression of the mercury in both cases, and that the effect due to the ether is much greater than that caused by the water. Measure the levels again, and find the **vapour pressures** of the two liquids at the atmospheric temperature. Warm the tube containing ether with the hand and notice the further fall of the mercury, due to the increase of vapour pressure with temperature.

The vapour pressure of a liquid rises very rapidly with the temperature. This is evident from Fig. 53, which is the **vapour pressure curve** of water. When the vapour pressure becomes equal to the *total* pressure exerted on the surface of the liquid, say by the atmosphere, the liquid **boils,** *i.e.*, vapour is emitted in bubbles throughout the whole bulk of the liquid. The **boiling point** of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure, or other total pressure, acting on the surface of the liquid. Boiling points are usually given for a pressure of 760 mm., or 1 standard atmosphere.

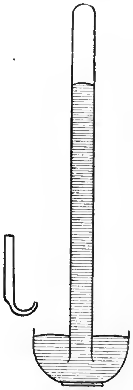

FIG. 52. Vapour Pressure of a Liquid in a Vacuous Space.

If the pressure on the surface is reduced, say by connecting a flask containing the liquid with a vacuum pump, the boiling point is depressed. Thus, under a pressure of 17·4 mm., water boils at 20°. It is therefore necessary to specify the pressure in giving a boiling point; unless this is done, it is understood that the pressure is 760 mm. Thus, the above result would be expressed as: 20°/17·4 mm. The boiling point of a pure liquid may be used as a means of characterising the substance (*cf.* p. 3).

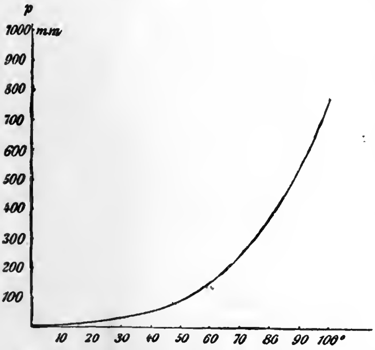

FIG. 53.—Vapour Pressure Curve of Water.

EXPT. 46.—The effect of pressure on the boiling point may be shown by boiling water in a strong round-bottomed flask, corking the flask, and placing it in cold water. Owing to the condensation of steam in the upper portion of the flask the pressure is reduced, and the water boils vigorously. This experiment is due to Bishop R. Watson.

The vapour pressure of a liquid is the same in a vacuum as in a space filled with an indifferent gas.

EXPT. 47.—Place a small sealed thin glass bulb, containing 2 c.c. of bromine (Fig. 54) inside a 500 c.c. bottle. Fit a rubber stopper to the bottle, through which pass a glass tube, closed at one end, and with the other end over the point of the bulb below, and a small manometer, containing mercury. Depress the tube so as to fracture the bulb, and observe the rise of pressure indicated by the manometer. Notice the formation of a layer of red bromine vapour in the lower part of the bottle. This diffuses upwards and the pressure rises as the space becomes saturated.

Vapour pressures of solids.—Not only liquids but also **solids** possess definite vapour pressures at different temperatures. These are usually smaller than those of liquids, although solids may have, at a given temperature, greater vapour pressures than liquids of different composition.

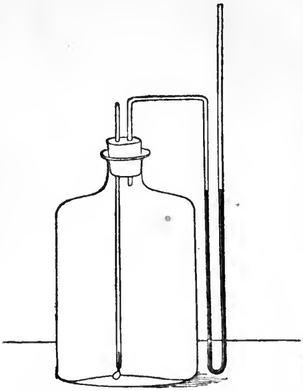

FIG. 54.—Vapour Pressure of a Liquid in a space filled with Gas.

EXPT. 48.—Pass a small piece of **camphor** into the vacuous space in the barometer tube (Expt. 45) surrounded above by a hot-water jacket, and notice the fall of the mercury. Determine the vapour pressure of camphor, and compare it with that of water at the same temperature.

The vaporisation of solids without previous fusion is called **sublimation.**

Equilibrium.—At a given temperature, liquid (or solid) and vapour can exist indefinitely in contact when the pressure of the vapour is equal to the maximum vapour pressure at that temperature. The vapour is then **saturated.** Under these conditions the system composed of the two phases, liquid and vapour, is said to be in **equilibrium.** An equilibrium state is one which is independent of time. If we represent transition from liquid to vapour by the symbol: [Liquid] $\rightarrow$ [Vapour], *i.e.*, **evaporation,** and transition from vapour to liquid by: [Vapour] $\rightarrow$ [Liquid], *i.e.*, **condensation,** the state of equilibrium will be represented by [Liquid] $\rightleftarrows$ [Vapour], or, more concisely, **Liquid $\rightleftarrows$ Vapour.**

Moist gases.—In the laboratory, gases are often collected over water, and if an accurate measurement of the volume of the gas is to be made, it is necessary to correct for the water vapour it contains.

If water evaporates into a dry gas at constant pressure, the gas will expand. The volume of a given mass of gas is therefore *greater* when it is moist than when it is dry.

Suppose we have a volume of 100 c.c. of moist air, measured over water at 15°, and under a total pressure of 760 mm. This total pressure is, by the law of partial pressures, the sum of the pressure of the dry air and of the maximum vapour pressure of water at 15°, viz., 12·7 mm. The pressure of the dry air is therefore $760 - 12 \cdot 7 = 747 \cdot 3$ mm. If the water vapour were removed by a drying agent from the 100 c.c. of moist air contained in a closed vessel, the pressure would therefore fall to 747·3 mm. If we now increased the pressure of the dry air to 760 mm., the volume would become, by Boyle's law, $100 \times \frac{747 \cdot 3}{760}$ c.c., and at 0° this would be $100 \times \frac{747 \cdot 3}{760} \times \frac{273}{288} = 93 \cdot 2$ c.c.

In general, if a mass of gas *saturated* with moisture at $t°$ under a total pressure of P mm. occupies V c.c., the volume of *dry* gas at S.T.P. will be :

$$V \times \frac{P - f}{760} \times \frac{273}{273 + t} \text{ c.c.,}$$

where f is the vapour pressure of water at $t°$.

If partially saturated gases are measured over mercury, they may be saturated with water vapour by introducing a few drops of water into the measuring tube. This only applies, of course, to gases which are not appreciably soluble in water.

In using this formula we require a table of the **vapour pressures of water** at different temperatures. A portion of such a table is given below.

TABLE OF VAPOUR PRESSURES OF WATER.

Temp.	Vapour pressure in mm. mercury.	Temp.	Vapour pressure in mm. mercury.	Temp.	Vapour pressure in mm. mercury.	Temp.	Vapour pressure in mm. mercury.
0°	4·569	17°	14·39	30°	31·51	93°	588·3
5	6·534	18	15·33	40	54·9	94	610·6
10	9·140	19	16·32	50	92·0	95	633·7
11	9·77	20	17·36	60	148·9	96	657·4
12	10·43	21	18·47	70	233·3	97	681·9
13	11·14	22	19·63	80	354·9	98	707·1
14	11·88	23	20·86	90	525·5	99	733·2
15	12·67	24	22·15	91	545·8	100	760·0
16	13·51	25	23·52	92	566·7	110	1075

Intermediate values in the practically useful ranges 0–25° and 90–100° may be obtained by *interpolation*, such as is used with logarithm tables.

EXAMPLE 1.—Find the vapour pressure of water at 15·4°.

Vapour pressure at 15° = 12·67 mm. Vapour pressure at 16° = 13·51 mm.

∴ difference for 1° = 13·51 − 12·67 = 0·84 mm., ∴ difference for 0·4° = 0·84 × 0·4 = 0·34 mm. ∴ vapour pressure at 15·4° = 12·67 + 0·34 = 13·01 mm.

EXAMPLE 2.—Find the volume, dry and at S.T.P., of 175 c.c. of air measured over water at 18° and 749 mm. atmospheric pressure.

$V = 175$; $P = 749$ mm.; $f = 15{\cdot}33$ mm. (from table); $t = 18°$.

$$\therefore \text{ required volume} = 175 \times \frac{749 - 15{\cdot}3}{760} \times \frac{273}{273 + 18} = 158{\cdot}5 \text{ c.c.}$$

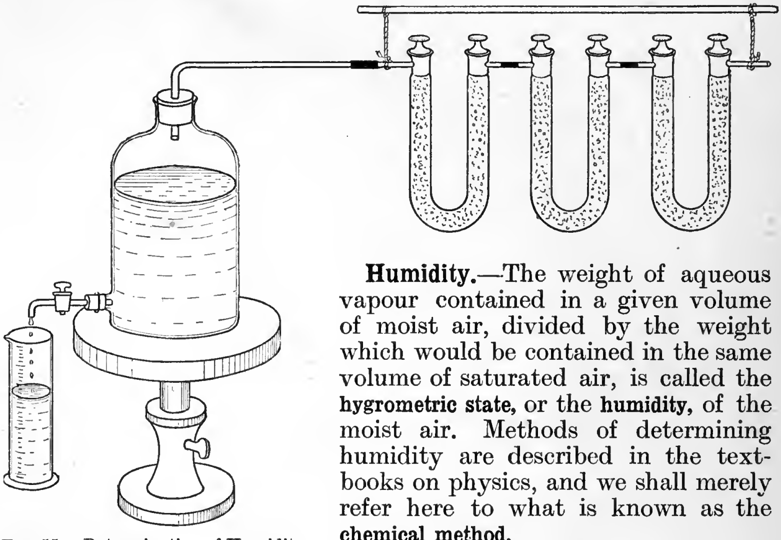

FIG. 55.—Determination of Humidity by the Chemical Method.

Humidity.—The weight of aqueous vapour contained in a given volume of moist air, divided by the weight which would be contained in the same volume of saturated air, is called the **hygrometric state,** or the **humidity,** of the moist air. Methods of determining humidity are described in the text-books on physics, and we shall merely refer here to what is known as the **chemical method.**

In this a known volume of air is drawn by means of an aspirator through a weighed series of U-tubes containing calcium chloride, or pumice soaked in sulphuric acid, which absorbs the moisture (Fig. 55). The weight of moisture in a given volume of air is thus found. Now it is known that the weight of 1 litre of aqueous vapour at S.T.P. (if it could exist at that temperature and pressure, and followed the gas laws) is 0·7962 gm. From the hygrometric experiment we should have found, however, that

x grams of aqueous vapour were contained in 1 litre of the air, and if we divide this by the amount contained when the air is *saturated* at $t°$, found from the table below, we obtain the **humidity.**

If the partial pressure of aqueous vapour in the air under given conditions is f', the weight in grams of water in 1 litre will be, at $t°$,

$$0{\cdot}796\dot{2} \times \left(\frac{f'}{760} \times \frac{273}{273+t}\right),$$

since the expression in brackets is the volume of vapour in litres at S.T.P., and the expression outside is the weight in gm. of 1 litre of aqueous vapour under these conditions.

If $f' = f$, the maximum vapour pressure, we obtain the table given below. It is easily seen that the **humidity** is given by the ratio f'/f.

Weight of Water Vapour in Grams in 1 Litre of Saturated Air

Temp. °C	Weight of Vapour	Temp. °C	Weight of Vapour	Temp. °C	Weight of Vapour	Temp. °C	Weight of Vapour	Temp. °C	Weight of Vapour
0 1	·0049 ·0052	21	·0182	41	·0533	61	·1348	81	·3073
2	·0056	22	·0193	42	·0560	62	·1407	82	·3128
3	·0060	23	·0204	43	·0588	63	·1468	83	·3246
4	·0064	24	·0216	44	·0618	64	·1532	84	·3368
5	·0068	25	·0228	45	·0648	65	·1597	85	·3493
6	·0072	26	·0241	46	·0681	66	·1666	86	·3623
7	·0077	27	·0255	47	·0714	67	·1736	87	·3756
8	·0082	28	·0270	48	·0749	68	·1809	88	·3894
9	·0088	29	·0285	49	·0785	69	·1885	89	·4035
10	·0094	30	·0307	50	·0823	70	·1963	90	·4180
11	·0100	31	·0317	51	·0862	71	·2044	91	·4330
12	·0106	32	·0335	52	·0902	72	·2127	92	·4454
13	·0013	33	·0353	53	·0945	73	·2213	93	·4643
14	·0120	34	·0372	54	·0989	74	·2302	94	·4806
15	·0127	35	·0393	55	·1034	75	·2395	95	·4974
16	·0135	36	·0413	56	·1082	76	·2490	96	·5146
17	·0144	37	·0435	57	·1131	77	·2588	97	·5323
18	·0152	38	·0458	58	·1183	78	·2689	98	·5505
19	·0162	39	·0482	59	·1235	79	·2794	99	·5693
20	·0171	40	·0507	60	·1291	80	·2901	100	·5884

The figures in the table have been calculated by the equation above.

The average humidity of the air in London during January is 0·7. Hence, when the temperature is 0°, the weight of moisture in 1 litre of such air is $0{\cdot}0049 \times 0{\cdot}7 = 0{\cdot}00343$ gm.

The law of partial pressures applied to vapours is not exact; the vapour pressure of a liquid in a gas is slightly *less* than *in vacuo*. It is only at low pressures, *i.e.*, at low temperatures, when the vapour pressures are small, that the application of the gas laws to vapours, made in the preceding equations, is justified. This is very nearly the case at the ordinary atmospheric temperature.

Density of a moist gas.—It may also be necessary to find the **density of moist air** (or other gas) of a given saturation at a given temperature. Consider 1 litre of moist air at $t°$, under a pressure P mm., and let f' be the partial pressure of aqueous vapour in the air. f' = *saturation pressure at* $t°$ (from table of vapour pressures) × *humidity*. The volume of the *dry* air at S.T.P. will be:

$$\frac{P-f'}{760} \times \frac{273}{273+t} \text{ litres,}$$

and since the weight of 1 litre of dry air at S.T.P. = 1·2928 gm. (p. 72), the weight of the dry air will be:

$$1{\cdot}2928 \times \frac{P-f'}{760} \times \frac{273}{273+t} \text{ gm.}$$

The volume of aqueous vapour at S.T.P. will be:

$$\frac{f'}{760} \times \frac{273}{273+t} \text{ litres,}$$

and since the (hypothetical) weight of 1 litre of aqueous vapour at S.T.P. is 0·7962 gm., the weight of the aqueous vapour in the 1 litre of moist air will be:

$$0{\cdot}7962 \times \frac{f'}{760} \times \frac{273}{273+t} \text{ gm.}$$

The total weight of the litre of moist air will therefore be:

$$1{\cdot}2928 \times \frac{P-f'}{760} \times \frac{273}{273+t} + 0{\cdot}7962 \times \frac{f'}{760} \times \frac{273}{273+t} \text{ gm.}$$

$$= \frac{273}{(273+t)\ 760}\left\{ 1{\cdot}2928\,(P-f') + 0{\cdot}7962 f' \right\} \text{ gm.,}$$

which is the density under the given conditions.

The same calculation applies to other moist gases, the appropriate density being used in place of 1·2928, the value for air.

Example.—Find the weight of 1 litre of hydrogen, saturated with moisture at 15°, and under a pressure of 740 mm.

Normal density of hydrogen = 0·08987 gm. per litre (p. 72) ; vapour pressure of water at 15° = 12·67 mm., hence required weight

$$= \frac{273}{(273 + 15)\,760} \left\{ 0{\cdot}08987\,(740 - 13) + 0{\cdot}7962 \times 12{\cdot}67 \right\}$$

$$= 0{\cdot}09417 \text{ gm.}$$

Note that, whereas moist air is lighter than dry air, the reverse is the case with hydrogen. This is because aqueous vapour is lighter than air but heavier than hydrogen.

Vapour densities.—Since vapours when far removed from their points of liquefaction obey approximately the same laws of expansion as gases, it is possible, if the weight of a known volume of vapour is determined at a given temperature and pressure, to reduce this volume to S.T.P. and so find the **normal density** of the vapour. This will be a hypothetical value, since the substance cannot really exist under such conditions, but it is the most convenient value for comparative purposes. The ratio of this number to the weight of 1 litre of hydrogen at S.T.P. is the **vapour density,** usually denoted by Δ.

The vapour density may also be found by dividing the weight of any volume of the vapour measured under the actual temperature and pressure of the experiment by the weight of an equal volume of hydrogen measured and weighed under the same conditions. The weight of V c.c. of hydrogen at a temperature $t°$ and under a pressure of P mm. is :

$$V \times 0{\cdot}00009 \times \frac{273}{273 + t} \times \frac{P}{760} \text{ gm.}$$

The vapour density of a volatile liquid or solid may be determined by one or other of the following methods ; that selected in any particular determination depends on the conditions of experiment, *e.g.*, whether a high or low temperature, or pressure, is used :—

(1) **Hofmann's modification of Gay-Lussac's method :** volume of a given weight of vapour is found.

(2) **Dumas' method :** weight of a given volume of vapour is determined.

(3) **Victor Meyer's method :** volume of air displaced by a given weight of vapour is determined.

Hofmann's method.—A. W. Hofmann (1868) surrounded a barometer tube with a glass jacket through which the vapour of a liquid boiling in a separate vessel was passed. Uniformity of temperature was thus assured. The liquid is weighed into a small bulb (Fig. 56) with a ground stopper, which is forced out under the diminished pressure when the bulb is passed into the upper part of the barometer tube. The latter is a wide tube, at least 1 metre in length, carefully graduated (Fig. 57). The liquid rapidly vaporises in the vacuous space above the mercury in the barometer tube; the bulb, of course, must be completely filled with the liquid, since a bubble of air will expand considerably in the vacuous space. The vapour jacket is provided with a side tube near the bottom for leading the vapour to the condenser.

FIG. 56. Bulb for Liquid.

The following liquids may be used in the boiler for supplying the vapour-jacket, the particular liquid taken depending on the boiling

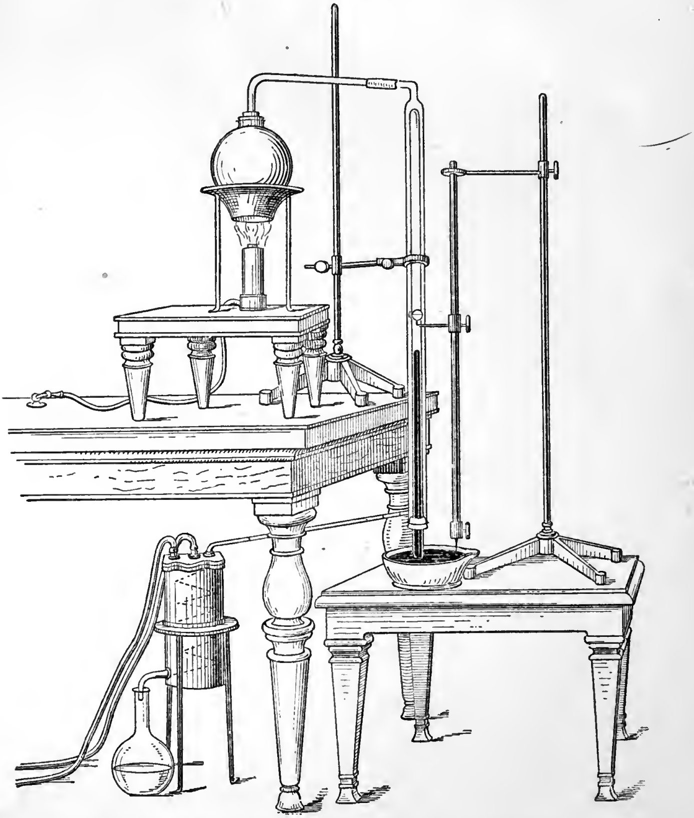

FIG. 57.—Hofmann's Method for Determination of Vapour Density of a Liquid.

point of the substance examined: the boiling points under 760 mm. pressure are stated:

Water, 100°	Toluidine, 202°
Amyl alcohol, 131–132°	Ethyl benzoate, 212°
Aniline, 181·5°	Amyl benzoate, 261°

Since volatilisation occurs more readily under diminished pressure, steam may often be used for the jacket in determining the vapour densities of liquids which boil under full atmospheric pressure as high as 180°. If the atmospheric pressure during the experiment differs appreciably from 760 mm., the boiling point of the liquid furnishing vapour to the jacket must be corrected by using special tables, or a thermometer may be hung in the vapour jacket.

When the mercury level is constant, the following data are noted:

(i) The volume of the vapour in c.c. = V.

(ii) The temperature, $t°$, in the jacket.

(iii) The pressure of the vapour; this is approximately given by the barometric height, H mm., *minus* the height of mercury in the tube above the level in the trough, h mm.; *i.e.*, $(H - h)$ mm.

In accurate work, the height of the *heated* mercury in the column in the tube must be reduced to 0°, to correspond with the corrected barometer reading, and allowance made for the expansion of the scale of the glass tube. The vapour pressure of mercury at the temperature of the jacket is also subtracted from the pressure of the vapour.

Let the weight of substance taken be m grams. The weight of a volume of hydrogen equal to that of the substance under the conditions of the experiment is

$$V \times 0{\cdot}00009 \times \frac{273}{273 + t} \times \frac{H - h}{760} = m' \text{ gm.}$$

The **vapour density**, Δ, is then m/m'.

Example.—0·338 gm. of carbon tetrachloride gave 109·8 c.c. of vapour in a Hofmann apparatus, at 99·5°. Barometric height = 746·9 mm. Height of mercury in tube above level in bath = 283·4 mm.

$$\therefore\ m' = 109{\cdot}8 \times 0{\cdot}00009 \times \frac{273}{372{\cdot}5} \times \frac{746{\cdot}9 - 283{\cdot}4}{760} = 0{\cdot}0044 \text{ gm.}$$

$\therefore$ vapour density of carbon tetrachloride = 0·338/0·0044 = **76·8.**

Dumas' method.—The method invented by Dumas (1827) is an extension of that commonly used for permanent gases (p. 69). Since the vapour does not come in contact with mercury, the method may be applied to substances (*e.g.*, bromine) which cannot be dealt with by Hofmann's method, and it may also, by the use of porcelain globes, be used at higher temperatures. It is not so accurate as the former method, and as the vaporisation is carried out under atmospheric pressure, and the temperature of the vapour is higher, it cannot be used for substances which readily decompose.

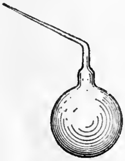

FIG. 58. Dumas' Vapour Density Bulb.

In Dumas' method a glass bulb (Fig. 58) of about 200 c.c. capacity, with a drawn-out neck, is cleaned, dried, and weighed. By warming the bulb, dipping the neck in the liquid to be examined, and cooling, sufficient liquid is introduced into the bulb to expel all the air when it is volatilised.

The bulb is then supported in an iron pot containing water, oil, or melted paraffin wax, heated 30–40° above the boiling point of the liquid, so that only the tip of the bulb projects above the surface of the liquid in the bath (Fig. 59). Volatilisation rapidly occurs, the air being expelled from the globe, and the vapour is at a temperature sufficiently above the boiling point to obey the gas laws with fair approximation. When the rush of vapour ceases, the neck of the globe is sealed off, and the temperature of the bath read off on the thermometer.

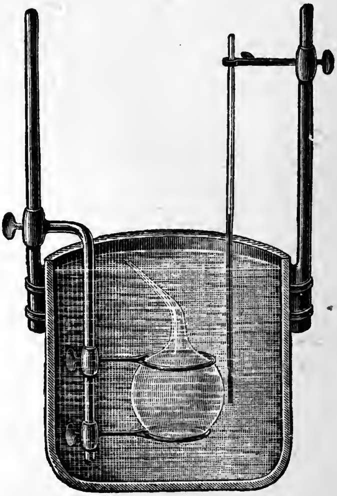

FIG. 59.—Dumas' Vapour Density Apparatus.

The globe is removed from the bath, cooled, cleaned, and reweighed along with the piece of neck sealed off. The neck is then scratched with a file, and the tip broken off under the surface of previously boiled water. The latter rushes into the bulb and, if the experiment has been successful, fills it completely. The bulb full of water is weighed, together with the two small pieces of the neck. The barometric pressures during the second weighing, and at the time of sealing, are noted.

Let the weight of the globe in air $= m$ gm.;
weight of the globe filled with vapour $= m_1$ gm.;
weight of the globe filled with water $= m_2$ gm.

The volume of the globe $= m_2 - m$ c.c.

The weight of air filling the globe at the temperature t, and pressure h, when it is weighed full of vapour, will be:

$$(m_2 - m) \times 0{\cdot}001293 \times \frac{273}{273 + t} \times \frac{h}{760} \text{ gm.} = A \text{ gm.},$$

hence the weight of the vacuous globe in air $= m - A$ gm., and weight of vapour filling the globe $= m' - (m - A)$ gm.

The weight of an equal volume of hydrogen at the temperature t' and pressure H of sealing will be:

$$(m_2 - m) \times 0{\cdot}00009 \times \frac{273}{273 + t'} \times \frac{H}{760} = m' \text{ gm.}$$

$$\therefore \quad \text{Vapour density } \Delta = \{ m_1 - (m - A) \} / m'.$$

In some cases the weight of vapour may be found by chemical methods. *E.g.*, if iodine has been used, the tip of the bulb is broken off under potassium iodide solution, which dissolves the iodine, and the solution is then titrated with sodium thiosulphate (p. 522).

EXAMPLE.—The vapour density of **hexane.**

Weight of empty globe in air = 23·449 gm.;
„ „ globe and vapour at 15·5° = 23·720 gm.

Temperature of sealing 110°; barometric pressure 759 mm., unchanged throughout the experiment. Capacity of globe, by weighing water, 178 c.c.

Weight of air displaced by globe

$$= 178 \times \frac{273}{288{\cdot}5} \times \frac{759}{760} \times 0{\cdot}001293 = 0{\cdot}2175 \text{ gm.},$$

$\therefore$ weight of vacuous globe $= 23{\cdot}449 - 0{\cdot}218 = 23{\cdot}231$ gm.,
$\therefore$ „ „ vapour $= 23{\cdot}720 - 23{\cdot}231 = 0{\cdot}489$ gm.

Weight of hydrogen filling globe at 110° and 759 mm.

$$= 178 \times \frac{273}{383} \times \frac{759}{760} \times 0{\cdot}00009 \text{ gm.} = 0{\cdot}0114 \text{ gm.}$$

Vapour density Δ = 0·489/0·0114 = 43·8.

The chief drawbacks to Dumas' method are the large quantity of substance required to displace the air of the bulb and the circumstance that, if the substance contains impurities of higher boiling point, these come off last and render the vapour sealed up impure, the density being too high.

Deville and Troost (1860) extended Dumas' method to higher temperatures by using globes of porcelain, heated in the vapours of mercury (357°), sulphur (444·6°), stannous chloride (660°), cadmium (778°), or zinc (918°), in an iron bath (Fig. 60), and sealing off the tip of the bulb with the oxy-hydrogen blowpipe. To find the temperature of the globe a companion globe filled with iodine, the density of which had been determined at various temperatures, was placed alongside the other globe. In this way the variation of the vapour density of many substances, *e.g.*, sulphur, with temperature (*cf.* p. 150) was found.

Victor Meyer's method.—Several new methods of finding vapour densities were devised by Victor Meyer, the most useful being the so-called **displacement method** (1878). This method is more rapidly and easily carried out than those of Dumas and Hofmann, requires only a small quantity of the substance, and gives quite accurate results.

A long glass tube with a bulb, *b* (Fig. 61), and a side tube, *a*, is heated in a long vapour bath, *c*, at a temperature which must be constant and higher than the boiling point of the substance, but need not otherwise be known. The tube *a* delivers into a graduated tube, *g*, in a trough of water. The tube *b* is heated in the bath until no more bubbles of air escape from *a*; then the latter is placed under the graduated tube, the cork, *d*, at the top of the long tube is taken out, and a weighed quantity of the liquid in a small stoppered bulb dropped into the heated bulb, the cork being quickly replaced. A little asbestos is placed in the bottom of the bulb, *b*, to prevent fracture on dropping in the bulb of liquid. It is also more convenient to drop in the bulb through a large bore stopcock instead of the cork at *d*.

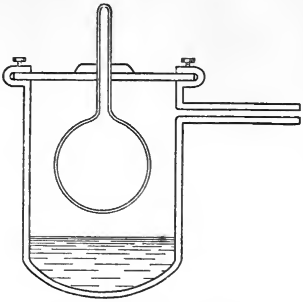

FIG. 60.—Vapour Densities at High Temperatures (Deville and Troost).

The substance quickly vaporises, and the vapour, which does not diffuse to the top of the narrow tube, displaces its own volume of air, which is collected in the graduated tube. When no more bubbles come off, the water levels in the tube and trough are equalised and the volume of air is read off.

Let the volume of moist air at the temperature $t°$ of the trough, and under a barometric pressure H, be V c.c. If the vapour pressure of water at $t°$ is f mm. (*cf.* table on p. 77), the volume of dry air at S.T.P. will be:

$$V \times \frac{273}{273+t} \times \frac{H-f}{760} \text{ c.c.} = V_0 \text{ c.c.}$$

This is the volume which the *vapour* of the given weight of substance would occupy at S.T.P. if it could exist under these conditions. The weight of an equal volume of hydrogen is $0{\cdot}00009\ V_0$ gm., so that if m gm. of substance were used, we have simply:

$$\textbf{Vapour density } \Delta = m/0{\cdot}00009\ V_0.$$

Example. — 0·1008 gm. of chloroform expelled 20·0 c.c. of moist air at 15° and 770 mm. pressure. Vapour pressure at 15° = 13 mm.

∴ volume of dry air at S.T.P.

$$= 20 \times \frac{273}{288} \times \frac{770 - 13}{760}$$
$$= 18{\cdot}9 \text{ c.c.}$$

Weight of an equal volume of hydrogen = 18·9 × 0·00009 gm. = 0·00169 gm.

∴ **vapour density** of chloroform = 0·1008/0·00169 = **59·6.**

Victor Meyer's method is not suitable for substances which break up on heating, and decompose still further when under reduced pressure (*e.g.*, phosphorus pentachloride, p. 153), since, owing to admixture of the vapour with air in the bulb, the partial pressure of the vapour is reduced to an extent which is not known.

The following substances may be used in the **heating bath :** water (100°), amyl alcohol (132°), xylene (140°), aniline (181·5°), ethyl benzoate (212°), benzophenone (306°), diphenylamine (310°), mercury (357°), sulphur (444·6°), molten lead.

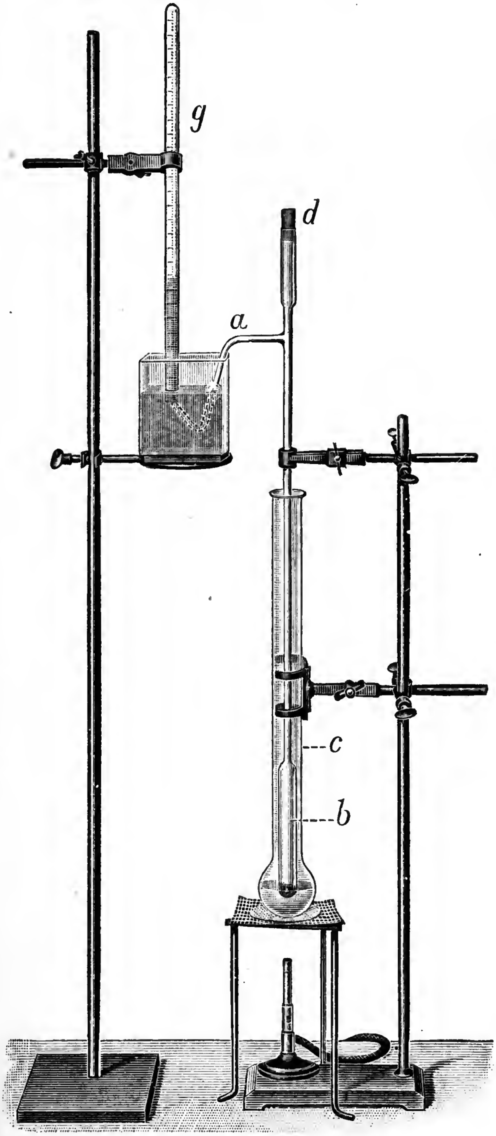

Fig. 61.—Victor Meyer's Vapour Density Apparatus.

Measurements by Victor Meyer's method at **high temperatures** were made by Nilson and Pettersson (1889), and later by Biltz and V. Meyer, who used bulbs of glazed porcelain, protected by wrapping them with thick platinum foil, placed inside graphite crucibles heated in a Perrot's gas furnace up to 1730°. By using water-gas in the furnace the temperature reached 1900°. The bulb is filled with inert gas (nitrogen, or argon) to prevent chemical action, and the substance, weighed out in a glass bulb, is dropped in as usual. Nernst (1903) used a small iridium bulb (3 c.c.), painted outside with zirconia, and heated electrically to 2000° in a small iridium tube. The substance (usually a fraction of a milligram) was weighed on a micro-balance sensitive to 1/2000 mgm., and the displacement measured directly by the movement of a drop of mercury in the horizontal graduated side tube (Fig. 62).

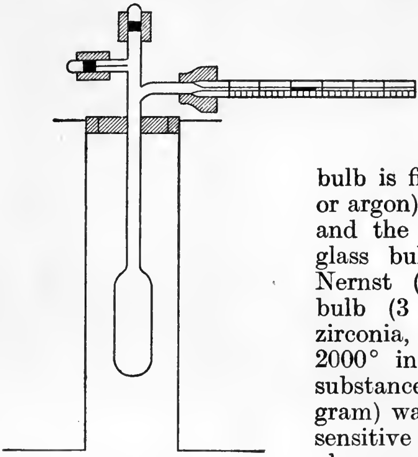

FIG. 62.—Nernst's Apparatus for Vapour Densities at High Temperatures.

A more sensitive **micro-balance**, sensitive to 1/500,000 mgm., was used by Ramsay and Gray (1911) in determining the density of radium emanation, 0·1 cu. mm., or less than 0·001 mgm., being used. It consists (Fig. 63) of a beam, *A*, of quartz rods, 10 cm. long, weighing 0·3 gm., with a quartz knife-edge, *B*, resting on a polished quartz plane, *C*. A small pan, *D*, and a sealed bulb, *E*, of known volume, both of quartz, are suspended from one end of the beam by a quartz fibre, and are counterpoised by a bead of fused quartz, *G*, on the other end of the beam. Oscillations are observed by a beam of light reflected from a mirror, *H*, through a glass window, *K*, in the air-tight metal case, *M*, on a scale several yards away. Weighings are made by altering the pressure of the air inside the balance case, and so changing

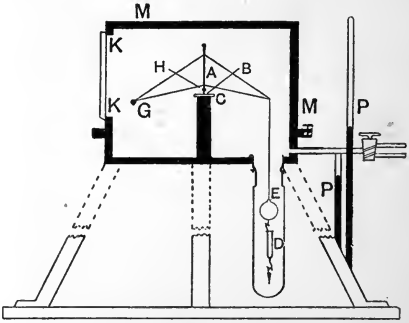

FIG. 63.—Micro-balance.

the buoyancy of the bulb, *E*. The pressure is measured by a manometer, *P*.

SUMMARY OF CHAPTER V

Physical properties of gases :—1. **Boyle's law** (1662): *when the temperature is constant the volume of a given mass of gas varies inversely as the pressure* : $v_1 : v_2 :: p_2 : p_1$, or **pv = const.**

2. **Charles's law** : *all gases expand by the same fraction*, $\frac{1}{273}$, *of their volume at* 0° C. *for* 1° *rise in temperature, when the pressure is constant* : $v_t = v_0\left(1 + \frac{t}{273}\right)$. If we put $T = t° + 273$, the **absolute temperature,** *the volumes at constant pressure* (*or the pressures at constant volume*) *are proportional to the absolute temperatures* : $v_1 : v_2 :: T_1 : T_2$. By combining this with Boyle's law we find : $pv/T =$ const.

3. The **normal density** of a gas is *the weight in grams of* 1 *litre* (1000·027 c.c.) *at* 0° *and* 760 *mm. pressure* (**standard temperature and pressure** = S.T.P.), *the weight being reduced to sea-level and latitude* 45°. The **relative density** of a gas (or vapour) is the ratio of the weight of any volume of the gas to the weight of an equal volume of hydrogen, under the same conditions. One c.c. of hydrogen at S.T.P. weighs 0·00009 gm.

4. **Dalton's law of partial pressures** : *if two or more gases, which do not interact chemically, are mixed in a vessel, the pressure of the mixture is the sum of the partial pressures*, i.e., *the pressures which would be exerted by each component if separately confined in the whole space occupied by the mixture.*

This applies (approximately) to vapours : the vapour pressure of a liquid is the same in a vacuum as in a space filled with an indifferent gas, and depends only on the temperature.

5. **Vapour densities** are determined by : (1) **Hofmann's method** (volume of a given weight found) : (2) **Dumas' method** (weight of a given volume found) ; (3) **Victor Meyer's method** (volume of *air* displaced by the vapour from a given weight of substance found under atmospheric conditions).

EXERCISES ON CHAPTER V

1. A volume of gas occupies 50 c.c. when measured over water at 15°. The barometric pressure is 747 mm. Find the volume of the dry gas at S.T.P. If the gas is oxygen, what would be its weight ?

2. A hydrogen cylinder of 2 cu. ft. capacity is filled by compression to 200 atm. If the gas is used in filling a balloon at atmospheric pressure, what volume will pass into the balloon ?

3. Two hundred c.c. of hydrogen and 50 c.c. of nitrogen, each measured at 15° and 760 mm., are admitted in succession to a previously exhausted 500 c.c. flask. What is the pressure of the mixture at 18° ?

4. Describe the method used in an accurate determination of the density of a gas. Explain the terms **normal density** and **relative density** as applied to gases. How may the relative density referred to hydrogen = 1 be converted into that referred to air = 1 ?

5. What methods are in use for the determination of vapour densities, and what are the advantages and disadvantages of each? Describe one method in detail.

6. In the determination of the vapour density of a substance by Dumas' method, the following data were obtained:

Weight of bulb in air = 44·7832 gm. Weight of bulb and vapour filling it at 115° = 45·1848 gm. Weight of bulb filled with water = 234·0 gm. Temperature of balance case = 12·8°. Barometric height = 75·1 cm. Find the vapour density.

7. In Victor Meyer's method it was found that 0·323 gm. of alcohol expelled 171·2 c.c. of air measured over water at 15·2° and 76·29 cm. Find the vapour density of alcohol.

8. What is meant by the *humidity* of air? It was found that 10 litres of air at 14·8° and 750 mm., when aspirated through calcium chloride tubes, caused an increase of weight of 0·1036 gm. Calculate: (i) the weight of 1 cu. m. of the moist air; (ii) the humidity.

9. Find the weight of 1 litre of hydrogen, saturated with water vapour at 15°, under 740 mm. pressure. If the pressure of the hydrogen is doubled, what is the weight of 1 litre of the moist gas?

CHAPTER VI

SOLUTIONS AND THE PHASE RULE

Equilibria between the phases of water.—It has been explained (p. 74) that if a quantity of liquid water is contained in a closed space it gives off vapour until a definite pressure is attained, for each temperature, known as the **vapour pressure.** When the vapour has attained the vapour pressure corresponding with the particular temperature, the liquid and vapour will exist together indefinitely, and are then said to be in **equilibrium.** This state of equilibrium between the two **phases** (p. 7) of water is denoted by the symbol: Water (liquid) $\rightleftharpoons$ Water (vapour).

In the same way, ice and water may co-exist in equilibrium at a particular temperature and pressure; thus, at 0° and under a pressure of one atmosphere (1·033 kgm. per sq. cm.) the two phases remain in contact without change for any length of time: Water (liquid) $\rightleftharpoons$ Water (solid). Since the vapour pressure of water varies with the temperature, we should expect the temperature at which ice and water co-exist also to be influenced by pressure, or, in other words, that the melting point of ice will depend on the pressure. It is found that the melting point of ice is *lowered* by pressure.

Expt. 49.—Hang a wire, carrying heavy weights at its ends, over a block of ice supported on a trestle. The wire gradually cuts its way through the block, since the ice melts beneath the wire, but the ice remains intact after the wire has passed through, because the water freezes again when the pressure is released on the ice becoming liquid.

The melting point of ice is lowered by 0·0073° by each additional atmosphere pressure. If snow is pressed between the hands it will cohere to a snowball unless it is very cold. In the latter case the degree of pressure which can be exerted by the hands cannot lower the melting point to the external temperature. Thus, if the snow is at $-10°$, a pressure of $10/0{\cdot}0073 = 1370$ atm. would be required. But in a hydraulic press a mass of transparent ice is formed. The fusion of ice under pressure, and its resolidification when the pressure is taken off, is called **regelation.**

Water in contact with vapour and water in contact with ice are heterogeneous systems, each composed of two phases. We denote the number of phases in a system by P.

Degrees of freedom.—We shall now explain what is understood by the number of **degrees of freedom** of a system, denoted by F.

If we have 1 gm. of water vapour at 100° confined in a cylinder under a piston, and if the pressure on the piston is always kept *below* 1 atm. or 1·033 kgm. per sq. cm., the vapour will behave more or less like a gas. (At very low pressures it will behave like an *ideal* gas: pressure × volume = const.) At all pressures less than 1 atm. the vapour is homogeneous, and at a given pressure and temperature it has a definite volume which, since 1 gm. has been taken, is called the **specific volume**, v. Now if we have the water vapour at a fixed temperature, under a fixed pressure, and with a fixed specific volume, it is **completely defined.** *E.g.*, it will have a definite heat capacity, a definite thermal conductivity, refractive index, etc. But if any *two* of the three independent variables, pressure, temperature, and specific volume, are fixed, the state will be completely defined, since the third variable will assume automatically a definite value. The same holds good if we have 1 gm. of liquid water in the cylinder. We express these results by saying that a **homogeneous system** composed of a pure gas or liquid has **two degrees of freedom** ($F = 2$), since *two* of the three variables may be arbitrarily fixed before the state is completely defined.

If the temperature of the water vapour remains at 100°, but the pressure is increased *above* 1·033 kgm. per sq. cm., then **liquid water** appears. The pressure now becomes constant, and remains equal to 1·033 kgm., as the piston descends, because the only effect of reducing the total volume is to cause vapour to turn into liquid. During this process the two phases (liquid and vapour) have constant temperatures and specific volumes, and each is under a constant pressure; hence they are both completely defined, and the system is in equilibrium. The only variable left is the temperature; if this is changed, the pressure and the specific volumes alter. In the same way, if to a mixture of ice and water we apply pressure, ice will melt, but the pressure and the specific volumes remain constant. A **heterogeneous system** of **two phases** ($P = 2$) of a pure substance has **one degree of freedom** ($F = 1$). The same is true if we have solid ice in contact with water vapour below 0°.

The triple point.—Ice, liquid water, and water vapour can exist together in equilibrium (with fixed specific volumes) only at one particular temperature (0·0077°), and under one particular pressure (4·57 mm. mercury). The heterogeneous system of **three phases** ($P = 3$) possesses **no degree of freedom** ($F = 0$), since it is completely defined only when *all* the variables, pressure, temperature, and specific volumes, are fixed. This state is known as the **triple**

point, and is defined by the values of the temperature and pressure : $t = 0{\cdot}0077°$, $p = 4{\cdot}57$ mm. Other pure substances (acetic acid, benzene) have different triple points.

Solutions.—We know that various kinds of **natural water** exist, such as rain water, river water, and sea water, which show different properties. If a natural water, *e.g.*, ordinary tap water, is evaporated to dryness in a platinum dish a white residue is left, showing that the water contained solid matter in **solution.** The residue from sea water is much larger than from the other forms of water, and consists mainly of common salt. The peculiar properties of sea water are due to the dissolved salt. Thus liquids, such as water, can hold solids in solution.

Dissolved solids are separated from liquids by the process of **distillation,** A simple apparatus for distillation consists of a glass retort with the neck passing into a glass flask, or receiver, which is cooled by a stream of cold water (Fig. 64). If tap water is distilled in this apparatus, the mineral matter remains in the retort, and **distilled water** collects in the receiver. If larger quantities of liquid are to be distilled it is more convenient to use a **Liebig's condenser** (Fig. 65), consisting of a glass tube enclosed in a jacket through which a constant stream of cold water is passed. The liquid to be distilled is contained in a **distilling flask,** provided with a side tube which is passed through a cork in the condenser. In the neck of the distilling flask a thermometer is supported by a cork, so as to enable the boiling point of the liquid to be determined.

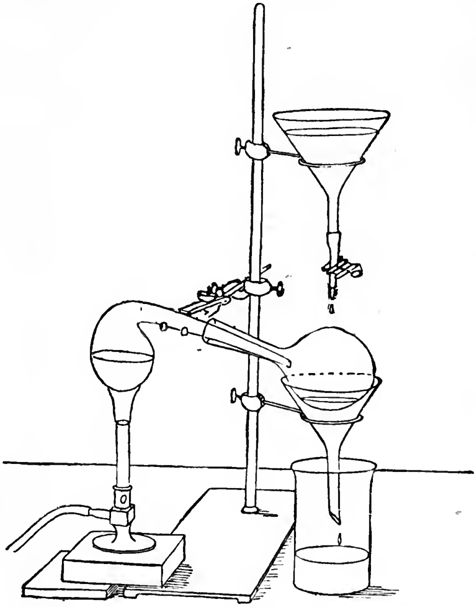

FIG. 64.—Retort and Receiver arranged for Distillation.

It is possible by means of distillation to separate not only **solutions of solids in liquids,** but also, at least partially, **solutions of liquids in liquids.** Thus, if a mixture of equal volumes of alcohol (b. pt.

78·3°) and water (b. pt. 100°) is distilled, it is found that the boiling point at the commencement of the operation is 84°. The liquid collecting in the receiver is richer in alcohol than the original mixture, and will burn when lighted in a dish. As the distillation proceeds, the boiling point rises, and the distillate contains more and more water. If the distillation is stopped when one-fourth of the mixture has distilled over, and the boiling point has risen to 85·5°, it will be found, if the distillate is poured into a clean flask and the operation repeated, that it begins to boil at 81·5°, *i.e.*, at a lower temperature than the original mixture, and the first portion of the distillate is correspondingly richer in alcohol. This partial separation of a solution of liquids by interrupted distillation is known as **fractional distillation.**

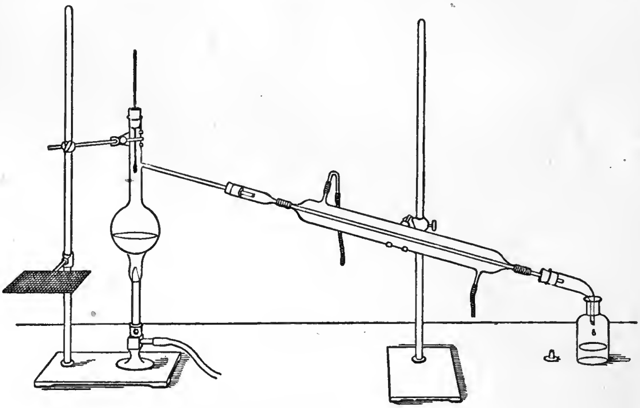

FIG. 65.—Distilling Apparatus with Liebig's Condenser.

If a flask and delivery tube are completely filled with tap water, and the flask is heated, bubbles of gas appear, which pass out of the delivery tube under water (Fig. 66), and will be found to be mainly air; such water therefore contains **dissolved gas.**

Thus, **liquids may hold in solution gases, liquids, and solids.**

Solids are capable of dissolving gases; thus palladium dissolves hydrogen (p. 71), forming **solid solutions.** Solids may also dissolve solids. Thus, if a piece of gold-leaf is pressed on a freshly-scraped piece of lead, the gold slowly penetrates into the latter, as may be proved by scraping off successive layers after a long time and analysing them. Many gem stones (ruby, sapphire, emerald) contain traces of metallic oxides, to which they owe their colour, in solution in a transparent, colourless mass of other substances.

True solutions are homogeneous (p. 9), and the dissolved substance is in an extremely fine state of subdivision. Thus, 1 gm. of eosin gives a distinct fluorescence (p. 8) to 1,000,000 c.c. of water when examined in a strong light. Each cubic centimetre of the solution contains only 0·000,001 gm. of the dye, and since a volume of only 10^{-12} c.c. of solution can be examined under the microscope, this can contain only 10^{-18} gm., or

0·000,000,000,000,000,001 gm. of dye.

Colloidal solutions, such as that of arsenic trisulphide (p. 12), pass through filter papers, and do not settle out on standing as suspensions of larger particles do; their heterogeneous character, however, is disclosed by the ultra-microscope. Colloidal solutions thus stand halfway between suspensions (separable by filtration) and true solutions (homogeneous even under the ultra-microscope). The radius of the particles of the dissolved substance in a true solution must be of the order of 10^{-8} cm. (*cf.* p. 9).

The substance present in larger amount in a solution, or the one which has the same physical state as the solution, is called the **solvent**; the other substance is called the **dissolved substance,** or the **solute.** Thus, a mixture of alcohol and water may be called a "solution of alcohol in water," or a "solution of water in alcohol," according as water or alcohol is in excess, but a very concentrated solution of sugar in water, containing more sugar than water, is always called a "solution of sugar in water," because water has the same physical state as the solution.

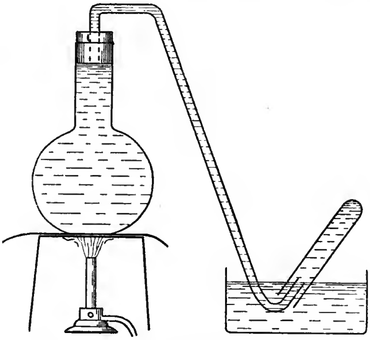

FIG. 66.—Expulsion of Dissolved Air from Water.

Solutions of gases in liquids: Henry's law (1803).—Solutions of gases (and vapours) **in gases** have already been considered in Chapter V, pp. 72, 74. The law of partial pressures applies to these cases, and asserts that the relation of the pressure to the concentration of one gas in a mixture is the same as if the other gases were not present.

Solutions of gases in liquids may be studied by the apparatus shown in Fig. 67, called an **absorptiometer.**

The gas is measured in the **burette,** *A*, over mercury, and the volume reduced to S.T.P. Part of the gas is then passed into the **absorption vessel,** *B*, the volume being found from that of the water run out, and is shaken with the liquid until the solution is **saturated,** *i.e.*, until the equilibrium [Gas] $\rightleftharpoons$ [Dissolved Gas] is established. The absorption vessel is then placed in a bath of water at a constant temperature, and the pressure adjusted by the levelling tube, *C*. The contraction in volume is then read off on the burette, and since the volume of water which was left in *B* is known, the number of c.c. of gas, reduced to S.T.P., which saturate 1 c.c. of water (or other solvent, *e.g.*, alcohol) can be calculated. This is called the **absorption coefficient.** The water used in the experiment must previously have been boiled to expel dissolved air, and cooled in a corked flask.

If the gas is very soluble (*e.g.*, ammonia, hydrochloric acid) it is bubbled through a measured volume of water until the latter is saturated. The amount of gas dissolved is then found by chemical analysis (*e.g.*, titration).

From the results of such experiments it has been found that the amount of gas dissolved by a fixed volume of liquid depends upon (1) the chemical composition of the gas and of the liquid, (2) the temperature, (3) the pressure. The effect of pressure is given by **Henry's law** (1803) : **the amount of gas absorbed by a liquid is proportional to the pressure.**

Since, however, the volume of a given amount of gas is inversely proportional to the pressure, it follows that *a given volume of liquid absorbs the same volume of gas at all pressures.* One c.c. of water absorbs 0·0489 c.c. of oxygen at 0° and 760 mm.; it absorbs twice this volume at 2 atm., or 2 × 760 mm., *if the gas is measured at S.T.P.* But this volume of gas still occupies 0·0489 c.c. under 2 atm. pressure.

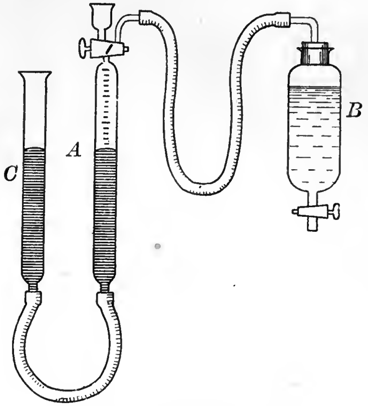

FIG. 67.—Absorptiometer.

Solubility of a mixture of gases in a liquid.—If we have to deal with the **solubility of a mixture of gases** in a liquid, the amount of any one gas dissolved is proportional to its **partial pressure,** when the gas has come into equilibrium with the liquid. This is **Dalton's extension of Henry's law.**

EXAMPLE.—The absorption coefficients of oxygen and nitrogen in water at 0° are 0·04890 and 0·023481, respectively. One hundred vols. of air contain 79·04 vols. of nitrogen and 20·96 vols. of oxygen. Hence the partial pressure of the oxygen is $\frac{20 \cdot 96}{100} = 0 \cdot 2096$ atm., that of the nitrogen $\frac{79\cdot04}{100} = 0\cdot7904$ atm., the sum of these being the total pressure, 1 atm. The volume of oxygen dissolved in 1 c.c. of water when agitated with air at 0° under 1 atm. pressure will thus be 0·2096 × 0·04890 = 0·010244 c.c., and the volume of nitrogen dissolved will be 0·7904 × 0·023481 = 0·018559 c.c. If the dissolved gas is now expelled by heating, its composition will thus be 0·010244 vol. of oxygen + 0·023481 vol. of nitrogen, *i.e.*, it will contain 64·4 per cent. of nitrogen and 35·6 per cent. of oxygen, by volume. It is therefore richer in oxygen than the original air. By shaking this gas again with water, and expelling the gas, the latter will be still richer in oxygen, until after eight repetitions a gas containing 97·3 per cent. of oxygen is obtained.

If the partial pressure of a gas above its solution be reduced to zero, all the gas will be expelled from the solution. This can usually be effected: (1) by reducing the pressure above the solution by an air-pump; (2) by passing a stream of indifferent gas through the solution (*e.g.*, nitrogen through aqueous ammonia); or (3) by boiling the solution, when the dissolved gas is driven off with the steam.

In some cases it is impossible to remove all the gas by boiling, etc.; this occurs when the gas and solvent evaporate *together* to form a vapour of the same composition as the solution; the latter then evaporates as a whole. *Cf.* p. 237.

Table of absorption coefficients.—Henry's law does not hold for very soluble gases, such as ammonia at the ordinary temperature, or hydrochloric acid, in water. It does not hold accurately for carbon dioxide. At 100° the solubility of ammonia follows the law. At higher pressures, also, deviations occur; with more soluble gases these begin at 2 atm. pressure, with less soluble gases the law holds up to about 10 atm. A few **absorption coefficients** are given below, in c.c. at S.T.P., absorbed by 1 c.c. of water under a pressure of 760 mm.

	0°	10°	15°	20°	30°	40°	50°	60°
Ammonia	1300	910	802	710	—	—	—	—
Hydrochloric acid	506	474	458	442	411	386	362	339
Chlorine	—	3·09	2·63	2·26	1·77	1·41	1·20	1·0
Carbon dioxide..	1·713	1·194	1·019	0·878	0·66	0·53	0·44	0·36
Oxygen	0·049	0·038	0·034	0·031	0·026	0·023	0·021	0·019
Nitrogen	0·0239	0·0196	0·0179	0·0164	0·0138	0·0118	0·0106	0·0100
Hydrogen	0·0215	0·0198	0·0190	0·0184	—	—	—	—

Solutions of liquids in liquids.—Some liquids, such as water and mercury, are practically, though probably not absolutely, **immiscible**; others, such as water and sulphuric acid, are **completely miscible.** In some cases, such as ether and water, each liquid dissolves a limited amount of the other, and the liquids are said to be **partially miscible.** If successive small quantities of ether are added to water, they at first dissolve completely. At a certain point, the water becomes **saturated** with ether; 100 gm. of water then take up 2·16 gm. of ether at 22°. If more ether is added, a lighter layer separates, and floats on the water solution. This is not pure ether, but contains 11 gm. of water per 100 gm. of ether. With further addition of ether (if the layers are shaken together), the composition of each layer remains constant, but the lower (aqueous) layer gradually disappears as more and more ether is added, until it finally vanishes, the whole liquid then having the composition of the upper layer. Unlimited further quantities of ether may now be added without any separation of the homogeneous liquid into layers.

The two liquid layers may be separated in a **separating funnel** (Fig. 15); the presence of ether in the lower aqueous layer may be shown by heating it in a test-tube, when the ether vapour given off may be kindled. The presence of water in the upper ether layer may be shown by dropping a bit of sodium into it, when hydrogen is evolved. (Pure ether has no action on sodium.)

The compositions of liquid layers in equilibrium at 22° is given below.

	Subst. in 100 gm. of water.	Water in 100 gm. of subst.
Ether	2·16 gm.	11·02 gm.
Chloroform	0·64 ,,	0·10 ,,
Carbon disulphide	1·24 ,,	0·13 ,,

The partition law.—If to the two layers of ether and water a little iodine is added, which dissolves in each pure solvent, it is found on shaking that the iodine is shared between the two liquids, but most of it, as is seen from the colours of the solutions, is taken by the ether. In such cases, where a solute is shared between two partially miscible or immiscible solvents, **the ratio of the solute concentrations in each layer is constant** at a particular temperature, independently of the absolute amounts of solute and liquids, or the relative amounts of the two layers. (The **concentration of a solution** is the weight of solute in 1 c.c. of solution.) The constant ratio is called the **ratio of distribution,** or the **partition coefficient,** and the result just stated, due to Berthelot and Jungfleisch (1872), is called the **distribution** or **partition law.**

If c_1, c_2 are the concentrations in the two layers, respectively, then:

$$c_1/c_2 = \text{const.} = k, \text{ or } c_1 = kc_2,$$

where k is the partition ratio.

Thus, at 25° an aqueous solution of iodine containing 0·0516 gm. per litre is in equilibrium with a solution of iodine in carbon tetrachloride containing 4·412 gm. of iodine per litre.

The **partition coefficient** is:

$$\frac{\text{concentration in carbon tetrachloride}}{\text{concentration in water}} = \frac{4\cdot412}{0\cdot0516} = 85\cdot5.$$

A saturated solution of iodine in water at 25° contains 0·340 gm. per litre. From the partition coefficient we can calculate the concentration of a solution of iodine in carbon tetrachloride in equilibrium with a saturated solution in water. This is 0·340 × 85·5 = 29·1 gm. per litre.

Solutions of solids in liquids.—The most important class of solutions is formed by dissolving **solids in liquids.** Common salt added in successive small amounts to water dissolves up to a certain point; after this no more salt passes into solution, but settles out unchanged. A solution which has dissolved as much solute as is possible under the given conditions (*e.g.*, at a fixed temperature) is called a **saturated solution**; it can exist in equilibrium with excess of solute: Salt [solid] $\rightleftharpoons$ Salt [dissd.]. The **concentration** of a solution of a solid in a liquid is expressed in various ways; usually as the number of grams of solute contained in 100 gm. of **solvent.** The concentration of a solution saturated with a solute is called the **solubility** of the latter; it is the maximum weight in grams of solid dissolved by 100 gm. of solvent at the given temperature, in presence of the solid salt. For common salt in water it is 35·9 at 15°. The solubility depends (1) on the chemical character of the solute and solvent, (2) on the temperature, and (3) to a slight extent on the pressure, in some cases (sodium chloride) increasing, in other cases (ammonium chloride) decreasing, with increase of pressure. The solubility of solids in water varies from that of such "insoluble" substances as barium sulphate, to that of very soluble substances such as calcium chloride. The very small solubilities of such solids as barium sulphate have actually been measured (p. 103).

The solubility usually increases with the temperature. In some cases, such as sodium chloride, it is nearly independent of temperature, and in others, such as calcium sulphate above 40°, it diminishes with rise of temperature.

Expt. 50.—The diminution of solubility with rise of temperature may be shown by placing a tube containing calcium butyrate solution, saturated at the ordinary temperature, in a beaker of boiling water. In a short time crystals of the salt separate. These redissolve on cooling.

The dependence of solubility on temperature is most conveniently represented graphically by means of **solubility curves**, in which the abscissæ represent temperatures, and the ordinates the solubilities. In Fig. 68 the solubility curves of some salts in water are exhibited. It will be seen that these show a great diversity

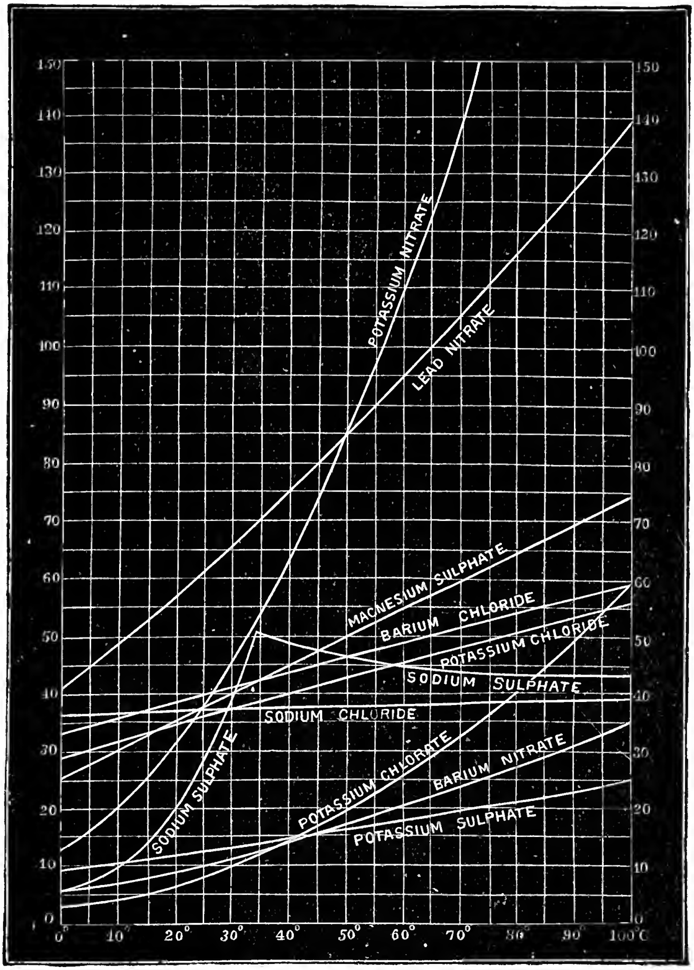

FIG. 68.—Solubility Curves.

Supersaturation.—If a saturated solution of a salt is evaporated, so as to drive off some solvent, and then allowed to cool, the salt will be present in amount greater than corresponds with saturation. Solid salt is then usually deposited in definite forms called **crystals.** Many salts crystallising from aqueous solutions form crystals of definite composition containing water. These are chemical compounds, called **hydrates.** The water of hydration is usually known as **water of crystallisation.** In many cases, however, when the solution after boiling is cooled, the salt is not deposited. The cooled solution then contains more salt than corresponds with saturation at the given temperature, and is said to be **supersaturated.** Crystallisation is at once induced by throwing a small crystal of the solid into the solution. It is found that **large crystals** are deposited when the crystallisation takes place slowly. The solution should not be too concentrated, and should be left at rest. Very large crystals of alum, for example, may be obtained by allowing a solution, saturated at the ordinary temperature, to evaporate slowly in the air, and suspending a small perfect crystal in the solution by a thread. If a very strong, hot solution is cooled rapidly, and stirred, **small crystals** are deposited. These are usually purer than the large crystals, since they are less likely to include liquid. Mother liquor is removed by pressing with a spatula on filter-paper in a Büchner funnel under reduced pressure. The mass is then pressed with filter-paper on a porous plate of unglazed earthenware, and finally dried in the air.

Expt. 51.—Heat on a water-bath 250 gm. of crystallised sodium thiosulphate (" hypo ") in a conical flask, the neck of which is plugged with cotton-wool. The salt melts in its own water of crystallisation, and forms a very concentrated solution. On cooling, this remains liquid ; it is then a **supersaturated solution.** Remove the plug and drop into the liquid a crystal of hypo. The liquid at once begins to solidify, and the mass becomes warm, since heat is evolved in the process. Supersaturated solutions invariably crystallise in contact with the solid form of the solute.

Expt. 52.—Fuse some crystals of hypo in a long test-tube, and pour over the liquid a supersaturated solution of sodium acetate, prepared by warming the crystallised salt with one-quarter its weight of water in a flask. Care should be taken to avoid mixing the liquids. Plug the tube with cotton-wool and allow to cool. Remove the plug and drop in a crystal of hypo. This falls through the acetate solution without inducing crystallisation, but on its reaching the hypo solution it brings about crystallisation of the latter. Now drop in a crystal of sodium acetate. The upper liquid then crystallises. Supersaturated solutions are caused to crystallise only by contact with the particular solid dissolved in them (or a solid isomorphous with this, see p. 442).

If a supersaturated solution is strongly cooled it may crystallise spontaneously, without contact with solid. Thus, if a supersaturated solution of hypo is cooled in a freezing mixture of Glauber's salt and concentrated hydrochloric acid, it crystallises spontaneously.

Determination of solubility.—The solubility of a salt at various temperatures is best determined by stirring the powdered solid salt with water at the given temperature, so that excess of solid is present, withdrawing a portion of the clear solution, weighing it, and then evaporating the solution in a weighed dish to find the weight of solid salt contained in it.

EXPT. 53.—A 25 c.c. pipette is fitted with pieces of rubber tubing at each end. The upper piece of rubber is closed by a clip, whilst the lower piece is connected with a short piece of tubing, packed with glass wool, to serve as a filter (Fig. 69). The pipette is cleaned and dried. A quantity of powdered potassium nitrate is now stirred with water in a 250 c.c. beaker, set in a water-bath, and the temperature kept at 20°, as shown by a thermometer in the beaker. The mixture of salt and water is best stirred by a small glass stirrer driven by a motor. When the mixture has been stirred for fifteen minutes, the filter is attached to the pipette, and solution drawn into the latter till the mark is reached. The filter is detached, and the solution run from the pipette into a weighed weighing bottle. The latter is stoppered, allowed to cool, and weighed. The solution is poured into a weighed porcelain dish, and any crystals are removed from the bottle, and washed into the dish, by hot water. The liquid is then evaporated on a sand-bath (spirting being avoided), and the dry residue weighed. The experiment is repeated at 30°, 40°, and 50°, and the **solubilities**, in grams per 100 gm. of water, plotted against the temperatures (Fig. 68).

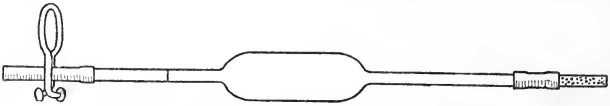
FIG. 69.—Pipette for Determination of Solubility.

Table of solubilities.—The solubility depends on the character of the **solid phase** in contact with the solution; in particular, salts crystallising with different proportions of water have different solubilities.

Thus, calcium sulphate occurs in two forms containing water. One of these is the mineral gypsum. If gypsum is heated to 120–130° it loses part of its water of crystallisation, forming plaster of Paris.

The latter is more soluble than gypsum, and forms with water a solution supersaturated with respect to gypsum. The latter is deposited, and more of the lower hydrate passes into solution. This goes on until the whole has solidified to a mass of interlacing crystals of gypsum (" setting " of plaster of Paris).

It will be seen from Fig. 68 that the solubility curves of sodium and potassium chlorides are straight lines ; in general, however, the solubility increases more rapidly than the temperature.

The great variation in solubility exhibited by different salts is shown by the following table, giving the weights of **anhydrous** salt, *i.e.*, salt free from water, saturating 100 parts of water.

Salt.	0°	15°	**100°**
Potassium iodide	127·5	140	208
,, bromide	53·5	62·5	104
,, chloride	27·6	32·4	56·7
Sodium chloride	35·7	35·9	39·0
Calcium chloride ($CaCl_2,6H_2O$) ...	60	30°100	60°137
Strontium chloride ($SrCl_2,6H_2O$)	43	50	—
Barium chloride ($BaCl_2,2H_2O$) ...	31·6	34·4	58·8
Potassium nitrate	13·3	25·8	246
Sodium nitrate	73·0	85	178
Barium hydroxide ($Ba(OH)_2,8H_2O$)	1·67	3·23	101·4 (80°)
Calcium hydroxide	0·185	0·170	0·077
Calcium sulphate ($CaSO_4,2H_2O$)...	0·18	40°0·279	60°0·260
Strontium sulphate	—	0·0011	—
Barium sulphate	—	0·00023	—
Silver chloride	—	0·00015	—
,, bromide	—	0·00001	—
,, iodide	—	0·0000003	—

The freezing points of solutions.—If salt, sugar, or any *soluble* substance is added to water, the **freezing point** of the latter is depressed, and for each salt the *depression is proportional to the concentration of the solution.* (Blagden, 1788.)

Sea water freezes at about − 2° ; Bishop R. Watson (1771) experimented with solutions of salt, exposing them to cold air : " in equal quantities of water were dissolved quantities of sea salt, increasing in the arithmetical progression, 0, 5, 10, 15, 20, etc. ; the times in which the solutions began to freeze, reckoning from the time in which simple water began, increased accurately in the same progression : hence it may be inferred, that, in salt of the same kind, the resistance to congelation is in the direct simple proportion of the quantity of salt dissolved : this conclusion cannot be extended to salts of different kinds, since water saturated with sea salt is more difficultly congealed than when saturated with various other salts, which it dissolves in greater quantities."

The solid separating when solutions freeze is usually **pure ice** : all the solute remains in the still liquid portion. Thus, freezing serves to separate the constituents of a solution, just as distillation enables us to achieve the same end (p. 93). The solution remaining will become increasingly richer in salt as more and more ice separates, and hence, by Blagden's law, the freezing point falls more and more as ice continues to be formed.

When the freezing point has fallen to a certain value, it becomes constant, and the whole of the solution then solidifies without further fall in temperature, both **ice** and **solid salt** then separating together in the proportions in which they exist in the solution. This minimum temperature was formerly called the **cryohydric temperature** ; the mechanical mixture of ice and solid salt separating was supposed to be a compound, and called a **cryohydrate** (Guthrie, 1874). Later experimenters showed, by microscopic examination and in other ways, that the supposed cryohydrates are mechanical mixtures, and they are now known as **eutectics,** the lowest temperature attainable on freezing the solution being called the **eutectic point.** In the case of common salt and water this is – 22°.

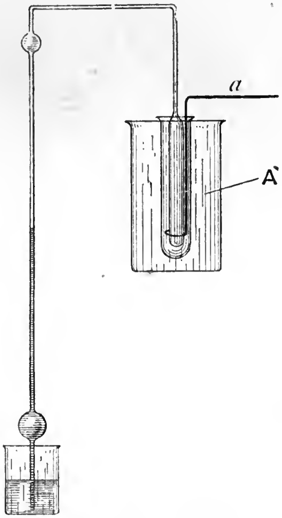

FIG. 70.—Depression of Freezing Point.

EXPT. 54.—The depression of freezing point by a dissolved substance may be shown in a lecture by the apparatus of Fig. 70. An air-thermometer bulb is placed in a large test-tube supported in a beaker. The tube of the air thermometer has two bulbs blown on it, and dips into coloured water. Water is first placed in the test-tube and a freezing mixture in the beaker. On stirring, the water freezes, and the height of liquid in the thermometer-tube is marked. One-hundred c.c. of an aqueous solution of 6 gm. of urea are now used. The liquid rises higher in the tube.

Vapour pressures of solutions.—If small drops of water are successively introduced into the vacuous space of a barometer-tube, surrounded by a water-jacket to keep the temperature constant, the following effects will be noticed. At first the level of the mercury falls after the addition of each drop, showing that **vapour** is being produced in the space, and is exerting a pressure (p. 74). After a certain number of drops have been added, **liquid** appears floating on the surface of the mercury, and the pressure then remains perfectly constant, even if more water is added. In the homogeneous vapour phase we can have different pressures at a given temperature; there are two degrees of freedom. As soon as liquid appears together with vapour, the pressure becomes constant, and equal to the maximum vapour pressure. In the system composed of two phases in equilibrium: Water [liquid] $\rightleftharpoons$ Water [vapour] there is only one degree of freedom. Now let a little common salt be passed into the tube. It dissolves in the water, and the vapour pressure of the latter is found to be slightly diminished. By adding further successive quantities of salt, the vapour pressure falls still further. Here we have a system composed of two phases, solution and vapour, in equilibrium, which shows two degrees of freedom instead of only one, as in the case of pure water. To what is the difference due?

It arises from the fact that the liquid phase is no longer a pure substance which has a definite vapour pressure at a given temperature, but is a solution of variable composition, the vapour pressure of which, just as the freezing point, depends on the concentration of dissolved substance.

By adding more salt, the vapour pressure falls progressively until a point is reached when the solution is just saturated with salt. The vapour pressure is once more constant, since further addition of salt has no effect on the concentration, but merely remains as an undissolved solid at the bottom of the solution. The appearance of this extra phase, solid salt, has therefore again reduced the number of degrees of freedom by one, since the pressure now depends on a single variable, the temperature. The latter alters the concentration of the solution in equilibrium with the solid, and the vapour pressure. When solid salt is present, there are two equilibria coexisting:

1. Water (vapour) $\rightleftharpoons$ Water (in solution).
2. Salt (solid) $\rightleftharpoons$ Salt (in solution).

In considering equilibrium states of solutions, therefore, an additional variable enters, which was not involved in the case of pure substance, viz., the **concentration.** In a solution of two substances we need, obviously, only one concentration in order to define the composition; the other is then fixed. Thus, if the solution contains x per cent. of one component, it must contain $100 - x$ per cent. of the other. The independent variables, pressure, temperature, and concentration, are really exactly analogous to those, pressure, temperature, and specific volume, for a pure substance, since in the latter case we could have taken, instead of the specific volume, its reciprocal, $1/v$, or the density, which is the analogue of concentration.

Components.—If we have a system composed of phases, some or all of which are solutions, or pure substances of different chemical composition not convertible into one another, we shall require a limited number of substances from which the chemical composition of every phase may be constituted. The *least* number of these substances is called the **number of components** of the system. Thus, each of the three phases forming the triple point of water can be composed of a single substance, water; the systems formed from salt and water contain phases all of which can be built up of one or more of *two* components, salt and water.

The phase rule.—Consider the following table, which summarises results previously described.

Number of components, C	*Number of phases, P*	*Number of degrees of freedom, F*	*Equilibria.*
1	2	1	Water (liq.) ⇌ Water (vap.)
1	2	1	Water (solid) ⇌ Water (vap.)
1	2	1	Water (solid) ⇌ Water (liq.)
1	3	0	Water (solid) ⇌ Water (liq.) ⇌ Water (vap.)
2	2	2	Salt (dissd.) ⇌ Salt (solid)
2	2	2	Water (in sol.) ⇌ Water (vap.)
2	3	1	Water (in sol.) ⇌ Water (vap.) Salt (dissd.) ⇌ Salt (solid)

In all these cases we remark that a simple relation exists between the number of phases, of components, and of degrees of freedom, viz.,

Number of phases + Number of degrees of freedom = Number of components + 2.

This relation is perfectly general, and applies to all heterogeneous systems in equilibrium; it is called the **phase rule** (Willard Gibbs, 1876). If we denote the **number of phases** (p. 7) by P; the **number of degrees of freedom,** or the least number of independently variable magnitudes (temperature, pressure, and concentrations) which must be arbitrarily fixed before the state of equilibrium of the system is completely defined, by F; and the **number of components** by C, then:

$$P + F = C + 2.$$

Examples on the phase rule.—The following examples, to which the phase rule may be applied, are recapitulated. It will be seen that the rule is of great value in dealing with solutions.

1. **Pure substance**; $C = 1$.
   - *a.* **Homogeneous** gas, liquid, or solid: $P = 1$, hence $F = 1 + 2 - 1 = 2$. Thus, temperature and pressure, or temperature and concentration (density), or pressure and concentration, must be fixed before the state of equilibrium is defined.
   - *b.* **Phases of a pure substance**; $C = 1$.
     - (i) Solid$\rightleftarrows$Liquid, or Solid$\rightleftarrows$Vapour, or Liquid$\rightleftarrows$Vapour: $P = 2$, hence $F = 1 + 2 - 2 = 1$, *i.e.*, only temperature, or pressure, or one concentration, can be arbitrarily fixed before the state of equilibrium is completely defined.
     - (ii) Solid$\rightleftarrows$Liquid$\rightleftarrows$Vapour, *i.e.*, the triple point: $P = 3$, hence $F = 1 + 2 - 3 = 0$, *i.e.*, no single variable can be changed without causing complete disappearance of one phase from the system.

2. **Solutions**, say of two components; $C = 2$.
   - *a.* Gas$\rightleftarrows$Gas (dissd.): $P = 2$, hence $F = 2 + 2 - 2 = 2$, *i.e.*, temperature, pressure, or one concentration only can be fixed, and the system is then in equilibrium. We notice that the phase rule gives no indication of the way in which the concentration of the solution depends on the pressure, beyond the fact that it is fixed, at a given temperature, when the pressure of the gas is fixed. Henry's law gives a simple proportionality between pressure and concentration, but this holds only approximately, whereas the phase rule is quite general, and is not bound by approximate limitations.
   - *b.* Solid$\rightleftarrows$Solid (dissd.): $P = 2$, hence $F = 2 + 2 - 2 = 2$, *i.e.*, the solubility depends on the temperature and pressure. The effect of pressure, which is very slight, could have been predicted by the phase rule.
   - *c.* Solid$\rightleftarrows$Solution$\rightleftarrows$Vapour of Solvent: $P = 3$, hence $F = 2 + 2 - 3 = 1$, *i.e.*, a solution can be in equilibrium with solid and vapour only at a definite pressure (the pressure of the saturated vapour), and concentration (that of the saturated solution), at a given temperature.
   - *d.* Liquid I$\rightleftarrows$Liquid II, two partially miscible liquids, say ether and water, existing in two layers in absence of the vapour: $P = 2$, hence $F = 2 + 2 - 2 = 2$, *i.e.*, the composition of each layer is fixed at a given temperature and pressure. The influence of pressure on the miscibility is small; it is wholly eliminated if the vapour phase is present: $P = 3$, hence $F = 2 + 2 - 3 = 1$, *i.e.*, the degree of miscibility depends only on the temperature.

The eutectic point, the freezing points of solutions, and the effect of adding iodine to two layers of ether and water, may be considered by the reader.

The phase rule is seen to be at the same time very simple, and capable of very extensive application. In the latter, it has led to the jettisoning of a large bulk of speculative material which formerly occupied considerable space in the text-books of chemistry.

SUMMARY OF CHAPTER VI

A **solution** is a homogeneous phase formed from two or more pure substances, the composition being continuously variable within certain limits. All states of substances may form solutions.

Henry's law applies to *solutions of gases in liquids*, and states that *the solubility is proportional to the pressure.* It is an approximate law only. *The solubility of each constituent of a mixture of gases is proportional to its partial pressure* (**Dalton's law**).

Partition law: if a substance, *e.g.*, iodine, is shaken with two liquids, *e.g.*, ether and water, which are not, or are only partly, miscible, *the ratio of the concentrations of the dissolved substance in the two liquid layers is constant at a given temperature.* This ratio is called the **partition coefficient.**

The **freezing point** of a liquid is lowered by a dissolved substance, and *the lowering is proportional to the concentration.* This is true only if pure solid solvent separates on freezing.

The phase rule: *the number of components, C, of degrees of freedom, F, and of phases, P, in a heterogeneous system in equilibrium are related by the equation* $P + F = C + 2$.

EXERCISES ON CHAPTER VI

1. Define: phase, equilibrium, solution, solute, triple point, solubility. Describe a method by which you would determine the solubility of potassium chlorate in water at various temperatures.

2. State Henry's law. In what way would you proceed to test it in the case of carbon dioxide? Define *absorption coefficient.*

3. From the following data draw the solubility-curves of the salts:

gm./100 gm. water	0°	10°	20°	40°	60°	80°	100°
(*a*) Potassium nitrate...	13·3	20·9	32	64	110	169	246
(*b*) Glauber's salt	5·0	9·0	19·4	49	45	44	42
(*c*) Lithium carbonate	1·54	1·38	1·33	1·17	1·01	0·85	0·72

4. Define *partition ratio.* The partition ratio for iodine between carbon disulphide and water is 410 at a given temperature. On shaking an aqueous solution of iodine with carbon disulphide, 35·42 gm. of iodine were found per litre of the disulphide layer. Find the concentration of iodine in the aqueous layer.

5. State Gibbs's Phase Rule, and explain the terms used. Give four examples of its application.

6. What is a supersaturated solution ? Describe an experiment illustrating the production and properties of such a solution.

7. What are *cryohydrates*, and how are they produced ? What are they now usually called ?

8. Carbon dioxide is diluted with twice its volume of air, and shaken with water at 15°. What volume of carbon dioxide should be dissolved by 1 litre of water ?

9. What experimental evidence would you bring forward in support of the statement that "sea-water is a solution" ? How can it be separated into its constituents ? Give three methods which have been described for separating the constituents of solutions.

CHAPTER VII

THE LAWS OF STOICHIOMETRY

Stoichiometry.—That part of chemistry which deals with the **composition** of substances, by weight or volume, is called **stoichiometry,** this word being first used by Jeremias Benjamin Richter, in his "Anfangsgrunde der Stöchiometrie," or "Rudiments of Stoichiometry" (Breslau, 1792–4), to denote "the art of measuring the chemical elements," *i.e.*, their combining ratios.

The experimental laws deduced from a study of chemical composition are five in number; four relate to weights and one to volumes. They are called the **Laws of Stoichiometry,** or the **Laws of Chemical Combination:**

I. **The Law of Conservation of Matter,** without which there could be no quantitative investigation of material bodies (p. 19).

II. **The Law of Constant Proportions** (Proust, 1799).

III. **The Law of Multiple Proportions** (Dalton, 1803).

IV. **The Law of Equivalents** (Richter, 1792), sometimes called the **Law of Reciprocal Proportions,** or the **Law of Combining Weights.**

V. **The Law of Gaseous Volumes** (Gay-Lussac, 1808).

The first four laws will be studied in the present chapter; the law of volumes is considered in Chapter IX. All the laws have an experimental basis, and are quite independent of the Atomic Theory, which, however, gives a simple and rational explanation of them, as will be seen in the next two chapters.

The law of constant proportions.—This law, asserted by Proust in 1799, states that: **When combination between elements takes place, it is in definite proportions by weight, so that the composition of a pure chemical compound is independent of the way in which it is prepared.**

If x is the weight of an element X, y the weight of an element

Y, present in one specimen of a pure chemical compound of X and Y, the ratio x/y is the same in all other specimens of this compound.

"We must," says Proust, "recognise an invisible hand which holds the balance in the formation of compounds . . . a compound is a substance to which Nature assigns fixed ratios, it is, in short, a being which Nature never creates otherwise than balance in hand, *pondere et mesura.*"

This law may appear self-evident; it was not established, however, until a long and heated controversy between Proust and Berthollet had run its course. The latter chemist, a contemporary and acquaintance of Lavoisier, asserted in his "Chemical Statics" (1803) that the composition of a compound was variable, and dependent on its mode of preparation. He relied on the following experimental evidence:

1. A metal such as lead, when heated in air, absorbs oxygen in continuously increasing amounts up to a fixed maximum, corresponding with the formation of red lead, and the colour of the oxide, at first grey, passes through yellow to red by insensible gradations as the amount of oxygen increases.
2. A salt formed from a soluble acid and an insoluble base, such as sulphate of copper, may be precipitated with increasing amounts of a soluble base, such as potash, to form a continuous series of basic salts, in which the proportion of acid continuously diminishes. In the case mentioned, these form greenish-blue precipitates.
3. When mercury is dissolved in nitric acid, it unites with quantities of oxygen varying continuously from a minimum, when it forms mercurous salts, to a maximum, when it forms mercuric salts.
4. Aqueous solutions of sulphuric acid, salts, alcohol, etc., and metallic alloys and amalgams can be formed from their constituents in very variable proportions.

Proust was able to meet these objections one by one, and overturn them by experiment.

(1) The members of the supposed continuous series of metallic oxides were found to be **mixtures** of two, or a small number, of oxides, each of definite composition. Thus, the supposed **series of oxides of tin,** obtained by calcining the metal in air for varying periods of time, were all **mechanical mixtures of two definite oxides of tin,** possibly with some unchanged metal. These oxides were found by Proust to have the following compositions:

	1. Suboxide of Tin.	2. Protoxide of Tin.
Tin	87	78·4
Oxygen ...	13	21·6

The "oxide" of composition, tin 80, oxygen 20, for instance, prepared by Berthollet, was a mixture of 81·4 parts of protoxide with 18·6 of suboxide.

(2) The supposed basic salts of copper of variable composition were all hydrated oxide of copper, imperfectly freed from sulphate by washing.

(3) Mercury on dissolving in nitric acid forms only *two* salts: mercurous nitrate, formed when excess of metal is treated with cold dilute nitric acid, and mercuric nitrate, which is produced from the metal and excess of hot concentrated nitric acid. The other supposed salts were mixtures of these.

Berthollet was forced to recognise that in many cases substances of definite composition could be formed, but he regarded these as exceptional. In them the particular proportions of the elements gave the compound which was least soluble, or most volatile, or densest. Thus, "it so happens that salts separate out by crystallisation in the neutral state, because in the neutral state the insolubility is greatest."

The fifth class mentioned under Berthollet's evidence gave Proust a good deal of trouble. He replied by pointing out the difference between a **pure substance** and a **solution** (or mixture). He says:

> "Is the power which makes a metal dissolve in sulphur different from that which makes one sulphide dissolve in another? I shall be in no hurry to answer this question, legitimate though it be, for fear of losing myself in a region not sufficiently lighted up by the facts of science; but my distinctions will, I hope, be appreciated all the same when I say: The attraction which causes sugar to dissolve in water may or may not be the same as that which makes a fixed quantity of carbon and of hydrogen dissolve in another quantity of oxygen to form the sugar of plants, but what we do clearly perceive is that these two kinds of attraction are so different in their results that it is impossible to confound them."

Unfortunately, the matter is not always so simple; the alloys formed from mixtures of metals are sometimes simply mixtures of the metals, each of which has crystallised out separately on cooling; sometimes they are homogeneous solutions, and sometimes they contain definite compounds, of the metals. It is only comparatively recently that it has been possible to decide to which class a particular alloy belongs (Chapt. XXXVII). Proust was, therefore, wise in refusing to be in a hurry to answer this question.

The exactness of the law of constant proportions was established by the experiments of Stas (1865); Marignac (1860) had previously suggested that very slight differences might occur in the compositions of compounds made in different ways, but Stas's work showed that, if such differences existed, they did not exceed 1 part in 100,000, and were within the limits of experimental error.

Source of ammonia.	*Source of hydrobromic acid.*	*Source of silver*	*Ammon. bromide reacting with* 107·93 *of silver.*
1 Ammonium sulphate	Potassium bromide	Reduced with sodium formate	97·996 97·989
2 Potassium nitrite and zinc	Do.	Do.	98·001 97·990
3 Ammonium sulphate	Do.	Reduced with cuprous - ammon. sulphite	97·999
4 Do.	Pure bromine ...	Reduced with formate (*a*) unfused ... (*b*) fused on pure calcium phosphate ...	97·994 98·003
5 Ditto second crop of crystals, sublimed in pure ammonia gas and dried over sulphuric acid ...	Do.	Reduced with formate and fused on pure calcium phosphate ...	97·997
6 Same specimen of ammonium sulphate, but dried in hydrogen gas and ammonia gas at 180°	Same specimen as in (5)	Same specimen as in (5) ...	98·000
7 Silver bromide from 4 (*a*) reduced in hydrogen and the Silver fused (*a*) on calcium phosphate with hydrogen ... (*b*) on pure lime with hydrogen (did not appear perfectly bright and pure)			97·995 97·984

As an **example of the law of constant proportions,** the above results of Alexander Scott (1901) on the analysis of ammonium bromide may be quoted. Stas had been unable to obtain a specimen of this salt which remained perfectly white on heating; this was effected by Scott, who used perfectly pure ammonia and hydrobromic acid, prepared in different ways. The salt was then precipitated with silver nitrate made from different specimens of silver.

Isomerism.—The law of constant proportions asserts that a definite compound has a fixed chemical composition. The converse is not true: the same elements, combined in the same proportions by weight, may form two or more different substances, with characteristic physical and chemical properties. This property is known as **isomerism,** and the different substances of the same composition are called **isomers.** Chemical composition alone does not uniquely determine a pure substance.

Thus, red mercuric iodide, on heating to 126°, changes into a yellow form, of identical composition. This remains yellow on cooling, but changes into the red form when rubbed.

An element may also exist in various forms, which are called **allotropic modifications,** or **allotropes.** **Allotropy** is one form of isomerism.

Thus, sulphur, on heating, melts to a clear, mobile, pale yellow liquid. On further heating this is suddenly transformed into an orange-yellow viscous mass, which darkens as heating is continued, until at 440° it is almost black. The liquid is then less viscous, and if poured into cold water forms a brownish-yellow, transparent, sticky and elastic mass. On standing for a few days, this slowly becomes opaque, lemon-yellow, and brittle; it is reconverted into ordinary sulphur. Equal weights of crystalline and plastic sulphur, when burnt in oxygen, yield equal weights of the same substance, sulphur dioxide. They both consist of the same **element,** sulphur.

Isotopes.—The unique composition of a pure substance has come to be regarded as a self-evident fact. Soddy and Hyman (1914) found, however, that specimens of lead chloride, prepared respectively from thorium and uranium minerals containing lead, differed in composition by 1 part in 225, although they were identical in chemical properties. This startling result was confirmed by Richards and Lembert (1914). It appears that there are different varieties of lead, which combine in different proportions with chlorine. These different varieties of an element, which appear to be identical in chemical properties but may have different combining proportions, are called **isotopes.** Their existence, which extends to other elements besides lead, makes the question of the combining ratios of elements, and the definition of an element, much more difficult than was formerly supposed (see Chapter LI).

The Law of Multiple Proportions.—As a result of some theoretical speculations on the atomic constitution of matter, John Dalton, some time between 1802 and 1804, and probably in 1803, was led to assume that: **If two elements combine to form more than one compound, the weights of one element which unite with identical weights of the other are in simple multiple proportion.**

Although Proust was acquainted with different oxides of each of the metals, tin, copper, and iron, his analyses were not sufficiently accurate to disclose any simple relation between the weights of oxygen combined with identical weights of metal or *vice versa.* Thus, in the two oxides of tin (p. 111), the weights of tin combining with 100 parts of oxygen are in the ratio 1 : 1·87. According to Dalton's ideas, the ratio should be exactly 1 : 2, and he made further analyses to confirm this. Dalton's analyses were no more exact than the former, but those subsequently made by Berzelius established the accuracy of the law in question.

Dalton, by mixing 100 vols. of air with 36 vols. of nitric oxide over water in a narrow tube (5 in. × 0·3 in.), obtained a residue of 80 vols. of nitrogen after all the oxygen of the air had combined with the nitric oxide to form red fumes, which were absorbed by the water. But if the experiment was performed in a wide cylinder, 72 vols., *i.e.*, 36 × 2 vols., of nitric oxide could be added, 80 vols. of nitrogen again remaining. Thus, "... oxygen can combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity."

Analyses of **two oxides of nitrogen** by Davy, and of **two hydrides of carbon** by Dalton (1804), the latter results probably rounded off, also confirmed the law:

	Nitric oxide.	Nitrous oxide.
Nitrogen	79·8	164·8 = 79·8 × 2·06
Oxygen	100	100

	Marsh gas.	Olefiant gas.
Carbon	4·3	4·3
Hydrogen	2	1

The most striking example of the law of multiple proportions is furnished by **the five oxides of nitrogen.** The percentage compositions by weight of these five compounds are as follows:—

	Nitrous oxide.	Nitric oxide.	Nitrous anhydride.	Nitrogen dioxide.	Nitric anhydride.
Nitrogen ..	63·7	46·7	36·9	30·5	25·9
Oxygen ..	36·3	53·3	63·1	69·5	74·1

The weights of oxygen combined with 100 parts of nitrogen in these compounds are found by proportion, and are as follows:

57	114	171	228	285

If all these numbers are divided by the least, 57, we obtain the series:

1	2	3	4	5

Thus, the weights of oxygen combining with identical weights, 100 parts, of nitrogen to form the five compounds are in the simple proportion 1 : 2 : 3 : 4 : 5.

EXPT. 55.—Weigh out two portions of 6·35 gm. of iodine. Add one in small quantities at a time to 10 gm. of mercury in a small mortar, triturating the contents after each addition of iodine, and adding one or two drops of alcohol. The mixture of 10 gm. of mercury and 6·3 gm. of iodine is converted into a *green* powder (**mercurous iodide**). To this add a further 6·3 gm. of iodine and a few drops of alcohol, and triturate. The 10 gm. of mercury and 12·7 gm. of iodine give a *red* powder (**mercuric iodide**). Under the microscope, these two substances are seen to be homogeneous. Thus, in mercuric iodide the same weight of mercury is combined with *twice* the amount of iodine contained in mercurous iodide.

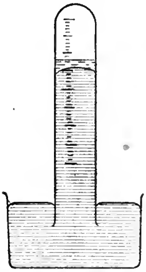
FIG. 71.—Experiment on Multiple Proportions.

EXPT. 56.—Wrap 0·5 gm. of bicarbonate of potash in tissue paper and pass it to the top of a graduated tube filled with mercury, the upper part containing 5 c.c. of concentrated hydrochloric acid (Fig. 71). Carbon dioxide is evolved. Heat 1 gm. of bicarbonate in a platinum crucible for a few minutes: it loses part of its carbon dioxide, forming carbonate of potash. If this is treated with acid, it evolves exactly the same volume of gas as the 0·5 gm. of bicarbonate. Hence the bicarbonate, on heating, loses exactly half its carbon dioxide in forming the carbonate.

Experiment 56 is due to William Hyde Wollaston (1808); in the same year Thomas Thomson showed that oxalic acid reacts with potash in two proportions, producing a neutral and an acid salt, and the acid oxalate requires, for identical weights of potash, exactly twice as much acid as the neutral salt. Wollaston discovered a third oxalate, and found the weights of oxalic acid reacting to be in the proportion 1 : 2 : 4. The law of multiple proportions therefore applies not only to elements, but also to compounds which interact chemically.

The **exactness** of the law of multiple proportions is well illustrated by the results of Stas (1849) and others on the composition of the

two oxides of carbon, carbon monoxide and carbon dioxide. Carbon dioxide was prepared by passing oxygen over a weighed amount of pure charcoal, diamond, or graphite, heated in a tube, and absorbing the gas in tubes containing caustic potash. Carbon monoxide was also oxidised to dioxide by passing it over red-hot copper oxide: carbon monoxide + copper oxide = carbon dioxide + copper.

One hundred parts of carbon dioxide were found to contain 27·278 parts of carbon. The weight of carbon monoxide yielding 100 parts of carbon dioxide was 63·640. Thus:

One hundred parts of carbon dioxide are produced from:
63·640 parts of carbon monoxide and 100 − 63·640 = 36·360 parts of oxygen.
27·278 parts of carbon and 100 − 27·278 = 72·722 parts of oxygen.

Again, 63·640 parts of carbon monoxide contain 27·278 parts of carbon and 63·640 − 27·278 = 36·362 parts of oxygen. Thus 27·278 parts of carbon are combined in carbon monoxide with 36·362 parts of oxygen, and in carbon dioxide with 72·722 parts of oxygen.

But 36·362 : 72·722 : : 1 : 1·99995, which differs from the exact ratio 1 : 2 by only 1 part in 40,000, *i.e.*, within the errors of experiment.

The law of equivalent proportions.—In 1766 Cavendish called a given weight of potash the **equivalent** of a (different) weight of lime when both neutralised identical weights of an acid. In 1788 he showed that the quantities of nitric and sulphuric acids which neutralised two identical weights of potash would also neutralise two identical weights of marble, different from those of the potash. This was the first clear recognition of **equivalent weights** of substances which interact chemically.

Experiments on the compositions of salts, and the proportions in which they interact chemically, were made by C. F. Wenzel, and published in his "Lehre von der Verwandtschaft der Körper" ("Theory of the Affinity of Bodies"), Dresden, 1777.* Wenzel was credited by Berzelius, apparently by an oversight, with the discovery of the law of equivalents. This is not confirmed by an examination of the book, which is written in an involved and obscure style.

In one experiment, Wenzel discusses the reaction between silver chloride and mercury sulphide, producing silver sulphide and mercuric chloride. He found that $\frac{1}{2}$ oz. of *luna cornea* (silver chloride) contained $180\frac{9}{16}$ grains of silver. From an analysis of silver sulphide ("geschwefeltes Silber"), he found that this $180\frac{9}{16}$ grains of silver are combined with $26\frac{3}{4}$ grains of sulphur. An analysis of *cinnabar* (mercuric sulphide) showed that $26\frac{3}{4}$ grains of sulphur form $125\frac{1}{2}$ grains of *cinnabar.*

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* There is a copy of this very rare book in the British Museum Library.

Now $\frac{1}{2}$ oz. of *luna cornea* contains $53\frac{7}{16}$ grains of "Salzsäure" (really chlorine), but by subtraction of the silver, $180\frac{9}{16}$ grains, from 240 grains, this amount would be $59\frac{7}{16}$ grains, instead of $53\frac{7}{16}$. An analysis of *corrosive sublimate* (mercuric chloride) showed that $53\frac{7}{16}$ grains of acid require $159\frac{2}{5}$ grains of mercury, and, from the analysis of *cinnabar*, this would correspond with $202\frac{1}{2}$ grains of *cinnabar*, instead of $125\frac{1}{2}$, as found in the first set of analyses.

Wenzel therefore remarks that: "$125\frac{1}{2}$ grains of cinnabar would not separate all the acid in the *luna cornea*." Further, if the mixture of cinnabar and *luna cornea* be sublimed, "the acid of the 'Hornsilber' (*luna cornea*) rises with the mercury out of $202\frac{1}{2}$ grains of cinnabar as a corrosive sublimate; the silver, on the other hand, remains combined with only so much sulphur as is contained in $125\frac{1}{2}$ grains of cinnabar." The inference is that the excess of sulphur remains uncombined. In other cases, Wenzel actually refers to uncombined residues from double decompositions, and suggests that they be used up by adding other substances. It therefore seems wide of the mark to suggest that Wenzel had any idea of the law of equivalents, or that his analyses were more exact than those of his contemporaries.

The generalisation of Cavendish's experiments is due to J. B. Richter, whose results are contained in his treatise on stoichiometry (see p. 110), 1792–4. Richter's reasoning is quite unnecessarily obscured by his attempts to derive mathematical relationships which do not exist; stripped of its verbiage, and exhibited in all its essentials, it appears in the German translation, by G. E. Fischer, of Berthollet's "Researches on the Laws of Affinity" (1802). In this the first **table of equivalent weights** of acids and bases is given, a portion of which is reproduced below.

Bases.		Acids.	
Alumina	525	Fluoric	427
Ammonia	672	Carbonic	577
Lime	793	Muriatic	712
Soda	859	Oxalic	755
Potash	1605	Sulphuric	1000
Baryta	2222	Nitric	1405

"The meaning of this table," said Fischer, "is that, if a substance is taken from one of the two columns, say potash from the first, to which corresponds the number 1605, the numbers in the other column indicate the quantity of each acid necessary to neutralise these 1605 parts of potash. There will in this case be required 712 parts of muriatic [hydrochloric] acid, 577 parts of carbonic acid, etc. If a substance is taken from the second column, the first column is to be used to ascertain how much of an earth or of an alkali is required to neutralise it."

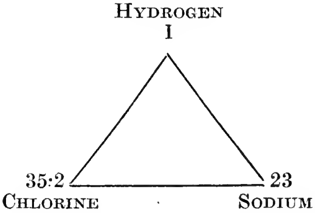
This table of twelve numbers enables us to calculate, by addition in pairs, the composition of thirty-six salts. By the analysis of six of the latter, say those corresponding with the constituents on the horizontal lines (*e.g.*, sulphate of potash), the compositions of the remaining thirty may be found.

Richter's result is a special case of the **law of equivalent proportions: the weights of two** (or more) **substances which separately react chemically with identical weights of a third are also the weights which react with each other, or simple multiples of them.**

An important case of the law is that which applies to the **combination of elements.** The **combining weights,** or **equivalent weights,** or simply **equivalents,** of the elements, are really the most fundamental values, since the equivalent weights of compounds are formed additively from those of their constituent elements.

Equivalents of the elements.—It is found that 23 gm. of **sodium** combine with 1 gm. of **hydrogen** to form **sodium hydride;** 35·2 gm. of **chlorine** combine with 1 gm. of **hydrogen** to form **hydrogen chloride.** The equivalent weights of sodium and chlorine, with respect to combination with hydrogen, are therefore 23 and 35·2, respectively. Now sodium and chlorine also combine together to form sodium chloride, and it is found that 23 parts of **sodium** combine with 35·2 parts of **chlorine** to form **sodium chloride.**

Thus, *the weights of sodium and chlorine which separately combine with* 1 *part by weight of hydrogen are the weights in which these two elements combine with each other.* This fact may be illustrated by the annexed diagram.



If 23 gm. of sodium are heated in hydrogen chloride gas, it is found that 1 gm. of hydrogen is displaced, whilst 35·2 gm. of chlorine combine with the 23 gm. of sodium to form sodium chloride. Thus, 23 parts of sodium can combine with 1 part of hydrogen, and can also *displace* it from its combination with another element.

The equivalent of an element is defined as that weight of it which combines with, or displaces, 1 part by weight of hydrogen.

Hydrogen is taken as the standard element for reasons of simplicity, because it is found that no element has an equivalent less than that of hydrogen.

The conception of an equivalent implies that, when once the equivalent of a single element has been determined with respect to hydrogen, the equivalent of that element may be used instead of hydrogen in the determination of other equivalent weights. Thus, having found that the equivalent of chlorine with respect to hydrogen is 35·2, we may use 35·2 parts of chlorine instead of 1 part of hydrogen in finding the equivalent of an element which combines with chlorine but does not combine with hydrogen. In the case of sodium, which combines with both hydrogen and chlorine, the equivalents are found to be identical. In other cases, the element may displace hydrogen but does not combine with it; *e.g.*, zinc, which evolves hydrogen from dilute acids, does not form a hydride. It is again found that the weight of such an element which combines with 35·2 parts of chlorine displaces 1 part of hydrogen. In the case of elements which neither combine with nor displace hydrogen, such as gold, the equivalent weight may be determined with respect to combination with chlorine, and is thus fixed in an indirect manner. The equivalents of such elements are then simply the weights which combine with or displace equivalent weights of other elements, which have been ascertained directly with respect to hydrogen.

The **equivalent of oxygen** may be calculated from the composition of water. In this way (p. 64) it is found to be 7·94. This number is of importance, since the equivalents of metals are sometimes determined with respect to oxygen, by converting the metal into the oxide. In this case, the equivalent is the weight combining with 7·94 parts of oxygen.

The **equivalent of a compound** is the sum of the equivalents of its constituent elements.

The determination of equivalents.—Equivalents are determined experimentally in various ways.

(1) The weight of the element combining with or displacing 1 part of hydrogen is found. This is applicable to metals which dissolve in acids, or alkalies, with evolution of hydrogen, the volume of which is measured.

(2) The weight of metal displaced from a solution of one of its salts by the equivalent of another metal, falling in class (1) is found. Thus, the equivalent of zinc is found by the measurement of the hydrogen evolved by zinc from an acid, and the equivalent of copper is then determined by weighing the copper displaced by the equivalent weight of zinc from a solution of copper sulphate.

(3) The weight of the element combining with 7·94 parts of oxygen is found; the combination may take place directly, as when magnesium is heated in air or oxygen, or indirectly, as when tin or copper is treated with nitric acid, and the product heated to redness. If the oxygen compound is decomposed on heating, *e.g.*, mercuric oxide, or potassium chlorate, the weight of oxygen liberated is found, and the equivalent of mercury, or of potassium chloride, *e.g.*, so determined.

(4) The weight of silver, the equivalent of which has been determined directly with respect to chlorine, required to precipitate a known weight of the chloride of an element, *e.g.*, potassium chloride, gives the equivalent of the latter.

(5) A given weight of one compound, composed of elements of known equivalents, may be converted into another compound, containing the element of which the equivalent is desired. Thus, potassium chloride is converted into potassium nitrate to determine the equivalent of nitrogen (those of potassium, chlorine, and oxygen being known.)

Since elements sometimes combine in more than one proportion, it follows that an element may have more than one equivalent. The law of multiple proportions then shows that **the different equivalents of an element are related in simple multiples.** Thus, carbon forms two compounds with oxygen, containing, for 7·94 parts of oxygen, 2·978 and 2·978 × 2 parts of carbon, respectively (p. 117).

EXPERIMENTS ON EQUIVALENTS

EXPT. 57.—Weigh out about 1 gm. of pure zinc into the small tube, *A* (Fig. 72). Lower this carefully into the dilute sulphuric acid (1 : 5 by vol.) in the flask, *B* (to which two or three drops of copper sulphate solution have been added), and fit the flask with the rubber stoppers, *C* and *C′*, to the bottle, *D*, containing about 1000 c.c. of water, previously filling the tube *E* with water and closing the pinchcock, *F*. When the flask, *B*, is in position open *F*. If the stoppers are tight, only a little water should run into the graduated cylinder, *G*, and this is poured out. Shake the flask, *B*, so as to bring the zinc into the acid. When the evolution of gas ceases, allow the apparatus to stand till the temperature is uniform; then, by raising or lowering *G*, bring the water levels to equality in *G* and *D*. Close the clip, *F*, remove the cylinder, and find the volume of gas evolved. Take the temperature of the water, read the barometer, and find the volume of hydrogen reduced to S.T.P. One c.c. of hydrogen at S.T.P. weighs 0·00009 gm. Find the weight of zinc which displaces 1 gm. of hydrogen, *i.e.*, the **equivalent**

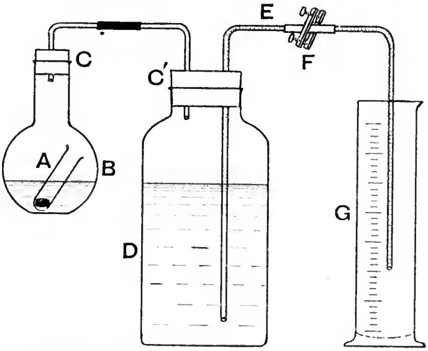


FIG. 72.—Apparatus for Determination of Equivalents.

of zinc. Repeat with iron (pure wire), magnesium (use very dilute acid), and aluminium (use strong caustic soda in *B*, and warm, if necessary). In each case find the equivalent of the metal.

EXPT. 58.—Weigh out 1–2 gm. of pure zinc and place it in a beaker containing a solution of copper sulphate, to which one or two drops of dilute sulphuric acid have been added. A red spongy deposit of copper is produced. When all the zinc has disappeared, filter through a weighed paper, wash the copper with hot water till the filtrate no longer becomes turbid with barium chloride (p. 12), dry in an air oven at 120°, and weigh. From the result of EXPT. 57, find the equivalent of copper. Repeat with magnesium and iron instead of zinc. From the value for copper found with zinc, calculate the equivalents of magnesium and iron, and compare with those found in EXPT. 57.

EXPT. 59.—Weigh out about 0·5 gm. of magnesium ribbon into a porcelain crucible with lid. Heat over a Bunsen burner until the metal has burnt into oxide, then remove the lid, and continue heating for ten minutes. Cool in a desiccator and weigh. Calculate the equivalent of magnesium, and compare with that previously found.

EXPT. 60.—Weigh out 1–2 gm. of pure tinfoil into a porcelain dish with a watch-glass cover. Add a few drops of concentrated nitric acid and replace the glass. Repeat till the action ceases, then heat *carefully* on a sand-bath till the excess of acid is driven off. Wash the oxide from the glass into the dish with a wash-bottle, and evaporate to dryness without cover, carefully avoiding spirting. Heat strongly for five minutes, cool in a desiccator, and weigh. Find the equivalent of tin (*cf.* p. 26). Repeat the experiment with copper.

Exact determination of equivalents.—The determination of the equivalents of a limited number of elements with all possible exactness was the life-work of the Belgian chemist J. S. Stas (1813–1891), whose numbers for carbon, nitrogen, sulphur, chlorine, bromine, iodine, lithium, sodium, potassium, lead, and silver were accepted for a number of years as the most accurate values, and regarded with almost superstitious reverence.

Stas began his researches with an analysis of potassium chlorate, which on heating gives off oxygen and leaves potassium chloride. Since the ratio *hydrogen/oxygen* was not certainly known at that time, Stas proposed as the basis of his numbers the **equivalent of oxygen,** which he took, not as 1, but as 8·00. He found that 127·2125 gm. of potassium chlorate gave on heating 77·4023 gm. of potassium chloride, hence the oxygen given off weighed 49·8102 gm. Potassium chlorate is known to contain 6 equivalents of oxygen, hence the **equivalent of potassium chloride,** x, is given by:

$$6 \times 8 : x :: 49{\cdot}8102 : 77{\cdot}4023, \quad \therefore x = \mathbf{74{\cdot}59}.$$

14·427 gm. of potassium chloride gave, on precipitation with silver nitrate solution, 27·733 gm. of silver chloride, hence the **equivalent of silver chloride** is given by the proportion:

$$74{\cdot}59 : x :: 14{\cdot}427 : 27{\cdot}732, \quad \therefore\ x = \mathbf{143{\cdot}37.}$$

101·519 gm. of pure silver when burnt in a current of chlorine gave 134·861 gm. of silver chloride, so that the **equivalent of silver** is given by the proportion:

$$143{\cdot}37 : x :: 134{\cdot}861 : 101{\cdot}519, \quad \therefore\ x = \mathbf{107{\cdot}93.}$$

Hence the **equivalent of chlorine** is 143·37 − 107·93 = **35·44,** and the **equivalent of potassium** is 74·59 − 35·44 = **39·15.**

The results of Stas may be summarised as follows:

Oxygen 8·00 (standard)	Silver 107·93
Chlorine 35·44	Potassium 39·15.

In 1895 Morley determined the ratio *hydrogen/oxygen* with great care and found 1 : 7·939; Scott (1893), and Burt and Edgar (1915), in most accurate researches, found 1 : 7·938. The equivalent of chlorine was determined directly (Dixon and Edgar, 1905, and Edgar, 1908), by the combustion of the gas in hydrogen, and weighing the hydrochloric acid, to be 35·186, with reference to hydrogen as unity. This number was exactly confirmed by a determination of the density of hydrochloric acid gas (Gray and Burt, 1909), and the decomposition of the latter by heated aluminium, with liberation of hydrogen. The equivalent of chlorine referred to oxygen = 8·00 is thus

$$35{\cdot}186 \times 8{\cdot}00 \div 7{\cdot}945 = 35{\cdot}463,$$

which differs from Stas's figure by as much as 1 in 1500.

This large discrepancy, confirmed by newer determinations, led to a suspicion that some at least of Stas's figures must be affected by systematic errors, and this was found to be the case. Even carefully recrystallised potassium chlorate always contains potassium chloride, and silver chloride, when precipitated from a solution of potassium chloride, always carries down some of the latter salt, which cannot be removed by washing.

The equivalents of the majority of the important elements are based on the equivalent of **silver. Oxygen** appears in few direct ratios. Since the equivalent of silver may be referred to that of hydrogen through the single intervening link of chlorine, *i.e.*, from the two ratios: *silver/chlorine*, and *chlorine/hydrogen*, both of which are very accurately known, **hydrogen** could more conveniently be adopted as a **practical standard** than oxygen. Its **theoretical advantages** are numerous. The fundamental derived unit, silver, cannot be referred directly to oxygen: on the oxygen standard, the value for nitrogen is involved as an intermediate link, since the ratio *silver / silver nitrate* is determined. But the most accurate value for nitrogen was derived from the analysis of ammonia, a hydrogen compound.

The single practical advantage of equivalents referred to oxygen = 8 is that in the case of a few common elements the numbers are more nearly whole numbers than is the case with hydrogen equivalents (p. 145).

SUMMARY OF CHAPTER VII

The **quantitative laws of chemistry** relating to weight (or mass) are: (1) **The Law of Conservation of Matter** (Chapter II); (2) **The Law of Constant Proportions** (Proust, 1799): *when combination between elements occurs, it is in definite proportions by weight*; (3) **The Law of Multiple Proportions** (Dalton, 1803): *when two elements form more than one compound, the weights of one element which combine with identical weights of the other are in simple multiple proportion*; (4) **The Law of Equivalent Proportions** (Richter, 1792): *the weights of two substances* (*e.g.*, elements) *which separately react* (*e.g.*, combine) *with identical weights of a third, are also the weights in which they react with each other, or simple multiples of them.*

The **equivalent** of an element is primarily defined as *the weight which combines with, or displaces, 1 part by weight of hydrogen.* The relation of equivalence may then be extended throughout the whole series of elements, including those which do not react with hydrogen. An element may have more than one equivalent: the law of multiple proportions then shows that the equivalents must be related as whole numbers, usually small.

EXERCISES ON CHAPTER VII

1. What are the laws of stoichiometry? State those relating to weight.

2. Give a short account of the nature and results of the controversy between Proust and Berthollet. What difficulty had Proust to explain after his work, and what account did he give of it?

3. Describe experiments to illustrate the laws of constant, multiple, and equivalent proportions. What is known as to the degree of accuracy of these laws?

4. 3·3665 gm. of zinc displaced 1212·09 c.c. of hydrogen, measured at 747·84 mm. and 10·73°, from dilute sulphuric acid. Calculate the equivalent of the metal.

5. 150·000 gm. of silver heated in sulphur vapour gave 172·2765 gm. of silver sulphide. 81·023 gm. of silver sulphate on reduction in hydrogen gave 56·071 gm. of silver. Assuming that the ratio *silver/sulphur* is the same in both compounds, and that silver sulphate contains 4 equivalents of oxygen, find the equivalents of silver and sulphur (Oxygen = 8).

CHAPTER VIII

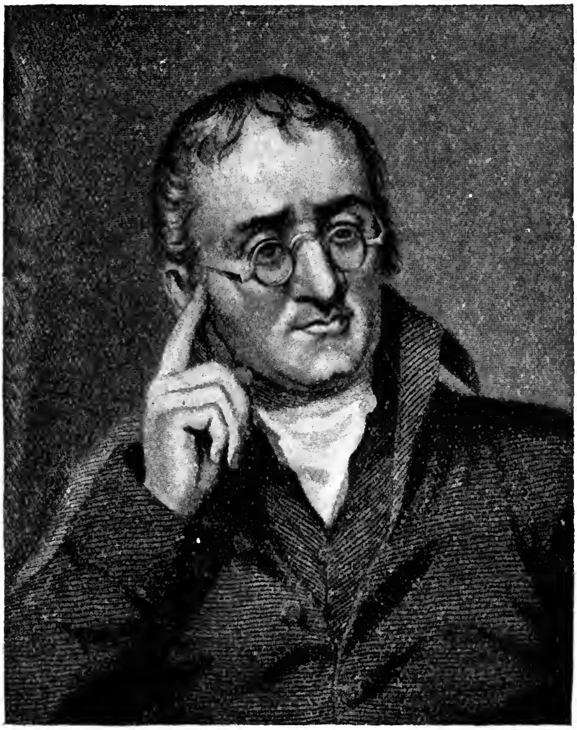
THE ATOMIC THEORY

Atoms.—The simplicity of the laws of chemical combination, or of stoichiometry, considered in the preceding chapter, leads inevitably to the conviction that they have their counterpart in some simple character of matter. The explanation of these laws presupposes some idea of the **structure of matter.** This may, no doubt, lie beyond the possibility of experimental apprehension, even when the observer is assisted by the most powerful of microscopes, and to this extent will remain a **hypothesis,** or a guess as to a possible cause. We shall see later, however, that an increase in the power of the ultra-microscope a hundred- or even ten-fold would bring us within reach of the direct perception of the underlying structure of material bodies.

Two possible guesses as to the ultimate structure of matter at once present themselves, and in fact originated in those distant times when history as we know it had scarcely begun. The first hypothesis sees matter as a continuous structure, completely filling the space occupied by bodies in the same way as jelly fills a mould. The second hypothesis sees matter filling space discontinuously, with interstitial gaps, much as small shot fills a barrel. The first view is associated with the Eleatic school, founded by Xenophanes (B.C. 576–480); the second is so much older that it is impossible to say where it originated. According to some it arose in India, about 1200 B.C., and passed to Greece, where it was taught by the old philosophers. Others think it originated with the Greeks themselves. This was the **atomic hypothesis,** which postulated the division of matter into exceedingly small particles, or **atoms,** incapable of further division by physical means.

Speculations on the atomic hypothesis occupied the Greek philosophers Anaxagoras, Leukippos, and Demokritus. Van Helmont, Lemery (1675), Boerhaave (1724), Boyle, and Newton (1642–1727) made more scientific use of the hypothesis; the last, although the author of the dictum *hypotheses non fingo,* was a thoroughgoing atomist. Newton gave a mathematical demonstration of Boyle's law on the basis of the hypothesis that gases consist of atoms repelling one another with forces inversely proportional to the distances. Boscovitch also made extensive application of a similar theory, but considered the atoms as mere points, or centres of force, endowed with mass.

Bryan, and William Higgins, in 1777 and 1789 respectively, made some applications of Newton's atomic theory to chemistry, but the merit of having independently elaborated a **chemical atomic theory** which was capable of co-ordinating all the known facts, and of being modified and extended with the progress of the science, belongs unquestionably to **John Dalton** (1766–1844).



JOHN DALTON.

John Dalton was born at Eaglesfield, a village near Cockermouth in Cumberland, and was throughout his life solely dependent upon his own exertions. As a boy he earned a living partly by teaching the rustic youth, and partly as a farm labourer. In 1781 he met Mr. John Gough, the blind philosopher of Kendal, whose influence on his life Dalton often gratefully recognised. After a period of study with Gough, including the writings of Newton, Dalton removed to Manchester, where the rest of his life was spent in scientific teaching and research. Dalton's manuscript note-books were discovered in the Archives of the Literary and Philosophical Society of that city by Roscoe and Harden in 1895, and from them it has been possible to trace, though imperfectly, the origin and development of Dalton's atomic theory. It unquestionably arose from the influence of Newton.

The origin of Dalton's atomic theory.—Apart from the influence of Newton, it is difficult to say what led Dalton to his atomic theory. Meldrum (1910) has shown that Dalton himself gave, at various times, four different accounts of its origin : (1) That communicated to his biographer, William Charles Henry, which attributed the theory to the influence of Richter, may be dismissed, since Richter is not mentioned in Dalton's note-books until 1807, whereas the atomic theory was certainly in existence in 1803, and probably in 1801–2. (2) Thomas Thomson's account, written after an interview with Dalton in 1804, was generally accepted before Roscoe and Harden's publication of the new facts, and attributed the origin of the theory to Dalton's attempt to explain the Law of Multiple Proportions, as exemplified by his discovery of the composition of marsh gas and of ethylene (p. 115). But the analyses of these gases were not made until 1804, whereas the first list of atomic weights was published in 1803. (3) Dalton's notes of lectures, given at the Royal Institution in 1810, trace the theory to some speculations on "mixed gases" (*i.e.*, on the law of partial pressures), made in 1801–2, and this is accepted by Roscoe and Harden, since it is the only account agreeing with the dates, and with the fourth source of information, viz. : (4) Dalton's manuscript note-books, preserved in Manchester.

It seems very probable that Dalton was led to his theory on purely *physical* lines ; it preceded the law of multiple proportions, and the latter was deduced from it. Dalton's experiments on multiple proportions appear to have been confirmatory only.

Dalton's atomic theory.—The **atomic theory** of Dalton, the great guiding principle of the whole of modern chemistry, is so simple that, as Lothar Meyer has said, "at first sight it is not illuminating." It asserts that :

(1) The chemical elements are composed of very minute particles of matter, called **atoms,** which preserve their individuality in all chemical changes.

Dalton was firmly convinced that these atoms are indivisible ; he was wont to say : "Thou knowest thou canst not cut an atom," and when referred to the sesquioxides (p. 134), which apparently contain $1\frac{1}{2}$ atoms of oxygen to 1 atom of the other element, replied: "but *they* are two to three," *i.e.*, 2 atoms of element to 3 atoms of oxygen.

(2) All the atoms of the same element are identical in all respects, particularly in **weight.** Different elements have atoms differing in weight. Each element is characterised by the weight of its atom.

The **absolute weights of atoms,** as Dalton realised, are very small indeed, and he therefore directed his attention to the determination of the **relative weights,** taking the weight of the lightest atom, that of **hydrogen,** as unity. The **atomic weight of an element** is then the number giving **the ratio of the weight** (or mass) **of an atom of that element to the weight** (or mass) **of an atom of hydrogen.**

If the absolute weight (or mass) of any *one* atom can be determined, those of all the others are found by simple multiplication of this by the ratios of the atomic weights. In recent years **the mass of the hydrogen atom** has been found by several different methods, giving results in surprising agreement (*cf.* p. 268). It is $\mathbf{1{\cdot}66\times10^{-24}}$ **gm.** Thus, 1 c.c. of hydrogen, at S.T.P., weighing 0·00009 gm., contains $5{\cdot}4 \times 10^{19}$ atoms. The weight of the heaviest atom known, that of uranium (atomic weight 236), is

$$236 \times 1{\cdot}66 \times 10^{-24} = 3{\cdot}92 \times 10^{-22} \text{ gm.}$$

(3) Chemical combination occurs by the union of the atoms of the elements in simple numerical ratios, *e.g.*, 1 atom A + 1 atom B; 1 atom A + 2 atoms B; 2 atoms A + 1 atom B; 2 atoms A + 3 atoms B, etc.

The aggregate of two or more atoms in a compound, called a "compound atom" by Dalton, is now named a **molecule** (*i.e.*, "a small mass"). A chemical compound *contains* its elements, since the atoms of these are present in the molecule, and may be recovered in the form of the original elements by decomposition. If mercury, for instance, is converted into the red oxide by heating in air, and the oxide then decomposed at a higher temperature, the *same* mercury is recovered as was used in the synthesis of the oxide.

Deduction of the laws of stoichiometry.—The empirical laws discussed in the last chapter follow as almost obvious consequences of the atomic theory.

(1) Since the atoms are indestructible in chemical changes, they preserve their masses in all such changes, and the mass of a compound is the sum of the masses of its elements. This is the **Law of Conservation of Mass,** or of **Matter** (p. 19).

(2) Just as all the atoms of an element are alike in all respects,

so also the molecules of a compound are identical, and are composed of the same number of atoms of the same elements. Thus, a compound has a unique composition. This is the **Law of Constant Proportions** (p. 110).

(3) If two elements combine in more than one proportion, the molecule of one compound must be formed by adding a whole number of atoms of one or both elements to one or more molecules of the other compound. This is the **Law of Multiple Proportions.**

(4) Compounds of the elements A and C must be formed according to the scheme: m atoms $A + n$ atoms C. Compounds of the elements B and C must be composed of: x atoms $B + y$ atoms C. Compounds of the elements A and B must contain: p atoms $A + q$ atoms B. But x, y, m, n, p, q are whole numbers, usually small. Hence p, q are either the same as m, x, or whole multiples of them, usually small. This is the **Law of Equivalent Proportions.**

The **equivalent** of an element will, from the definition, be either the **atomic weight** itself, or related to it in a simple manner, *i.e.*, it will be a simple fraction of it, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{2}{3}$, etc., since 1 atom of the element combines with 1, 2, 3, etc., atoms of hydrogen, or two atoms of the element with 3, 5, etc., atoms of hydrogen, and so on. In only one single case does 1 atom of hydrogen combine with more than 1 atom of another element, so that in all other cases the equivalent is either equal to, or *less* than, the atomic weight. The exceptional case is hydrazoic acid, a compound of 1 atom of hydrogen with 3 atoms of nitrogen. The equivalent of nitrogen in this compound is three times its atomic weight.

Limitations of Dalton's theory.—In its original form, Dalton's atomic theory provided no means of determining even the relative weights of the atoms. Thus, although 7·94 parts of oxygen combine with 1 part of hydrogen, we do not know how many atoms of each element the molecule of the resulting water contains. If it contains 1 atom of each element (as Dalton supposed), the atomic weight of oxygen is 7·94, but if it contains 2 atoms of hydrogen to 1 atom of oxygen, as the volume ratio would suggest, the atomic weight of oxygen is $2 \times 7{\cdot}94 = 15{\cdot}88$.

In general, if Q_1, Q_2 are the weights of two elements which combine together, we must have:

$$Q_1 : Q_2 : : a_1 A_1 : a_2 A_2,$$

where A_1 and A_2 are the atomic weights, and a_1, a_2 are whole numbers representing the numbers of atoms of each element, respectively, which enter into combination. Obviously, a knowledge of $Q_1 : Q_2$ alone does not enable us to find the ratio of the atomic weights, $A_1 : A_2$, unless the ratio of the numbers of atoms, $a_1 : a_2$, is also known.

Dalton himself was clearly aware of this deficiency, and was compelled to fall back on **empirical rules,** which he recognised as arbitrary. He assumed that, if only one compound of two elements is known, it is binary, *i.e.*, formed of one atom of each element. Thus, water was regarded as a compound of one atom each of hydrogen and oxygen, and ammonia as a compound of one atom each of nitrogen and hydrogen, since at that time no other compounds of these elements were known. This rule appears to have been connected with Newton's theory of the repulsion of atoms, according to which one atom of one element may be attracted by one atom of another element, but if two atoms of the same element are brought together they repel each other, and do not form a stable compound with a third atom. This reasoning had been used before by W. Higgins; it is given in Henry's "Chemistry" (1815), and since Henry was a personal friend of Dalton, he probably derived it from the latter. Although this rule as to the binary composition of a single stable compound had, therefore, some theoretical foundation, Dalton's further rules for the cases where more than one compound of two elements existed were purely arbitrary.

The work of Berzelius, who extended Dalton's investigations with great enthusiasm and success, led to no real improvement in this respect, since his skilful use of chemical analogies, although leading to the correct results in many cases, was equally arbitrary. Many chemists, therefore, whilst adopting the experimental basis of the theory, and the equivalent weights of elements, refused to attempt to derive the true atomic weights by mere rules. In particular, Leopold Gmelin, in his large "Handbook" (1817–19; English translation, 19 vols., 1848–72), reverted to the use of equivalents, and he had numerous followers. In other quarters an intolerable diversity of systems arose, dictated almost entirely by authority, and it began to appear as if the atomic theory had outgrown its usefulness.

Dalton seems to have assumed as self-evident that the particles of elements in the free state are single atoms. This was the main source of the difficulties of the earlier theory, since it is incorrect. The true theory, which would have resolved all the growing difficulties of Dalton's great generalisation, was given by the Italian physicist Avogadro, in 1811, but was entirely unheeded until it was revived in 1858 by his countryman, Cannizzaro. This theory forms the subject-matter of the next chapter.

Chemical nomenclature and notation.—The methods of naming chemical substances constitute chemical nomenclature; their representation by symbols is called chemical notation.

The **names of the metals** are derived from various sources. The association of the seven metals known to the ancients with the seven planets dates from the Babylonian period, and led to the alchemical names and symbols :

Gold (yellow) was called **Sol** (the Sun) and represented by ☼ or ☉ ; Silver (white) was named **Luna** (the Moon), ☾ ; Copper was named after **Venus,** ♀ ; Tin was **Jupiter** ♃ ; Iron was named after **Mars,** the God of War, ♂ ; **Mercury** (mobile) was named after the Messenger of the Gods, ☿ ; and Lead (dull and heavy) was **Saturn,** ♄. All these metals, except mercury, are referred to by Homer ; mercury is first mentioned by Aristotle (B.C. 384—322). The name Mercury still survives, and silver nitrate is often called *lunar caustic.*

The **nomenclature of the alchemists** was purely empirical, and a name frequently had one meaning to the adept and quite another to the ordinary man. The same substance had a variety of names, depending on its mode of preparation. Names were often based on accidental resemblances. Thus *butter of antimony* was classed along with ordinary butter, and *oil of vitriol* (sulphuric acid) with olive oil. Such names as *liver of sulphur* (impure potassium sulphide) and *cream of tartar* (potassium hydrogen tartrate) arose in this way. Salts were often named after their discoverers, or the places where they were found (Glauber's salt, Epsom salt).

A **scientific nomenclature** began with Macquer and Baumé, who, for instance, classed together the *vitriols,* or glassy, crystalline substances : *white vitriol* (zinc sulphate), *green vitriol* (ferrous sulphate), *blue vitriol* (copper sulphate). Bergman (1782) invented a more rational system of nomenclature which indicated the basic and acidic constituents of salts. *E.g.*, salts of potash, or the vegetable alkali, were named as follows :

vegetabile vitriolatum (potassium sulphate)
vegetabile nitratum (potassium nitrate).

The **modern chemical nomenclature** had its origin in a treatise ("Méthode d'une Nomenclature chimique," 1787) drawn up by Lavoisier, Berthollet, Guyton de Morveau, and Fourcroy, in order to make the antiphlogistic doctrines less dependent on names which had arisen during the phlogistic period.

The names of the elements.—Some of the elements (copper, gold, tin, sulphur) retain their old names ; newly discovered elements usually have names ending in **-um** if they are metals, and **-on** if they are non-metals (*e.g.*, potassium, and argon). (Selenium and tellurium were believed to be metals on their discovery ; helium was named before its isolation.) Many elements have names derived from Greek roots : **chlorine,** from *χγωρός*, *chloros*, greenish-yellow ; **bromine,** from *βρῶμος*, *bromos*, a stench ; **iodine,** from ἰοειδὴς, *ioïdes*, violet ; **chromium,** from *χρῶμα*, *chroma*, colour ;

helium, from ἥλιος, *helios,* the Sun, in the spectrum of which it was detected. Other elements have been named after mythological deities or personages : **vanadium,** from Vanadis, a cognomen of the Scandinavian goddess Freia ; **thorium,** from Thor, the Scandinavian war-god ; **tantalum** and **niobium,** from Tantalus and Niobe, of Greek mythology. The names of places where compounds of elements were first discovered have sometimes formed the bases of names : **strontium,** from Strontian, in Scotland ; **ruthenium,** from Ruthenia (Russia) ; **ytterbium,** from Ytterby (Sweden). **Beryllium** and **zirconium** are named after the minerals, *beryl* and *zircon,* which contain these elements. **Palladium** and **uranium** were called after the stars Pallas and Uranus, discovered about the same time, whilst **selenium** and **tellurium** are named after the Moon (*selene*) and the Earth (*tellus*).

The symbols of the elements.—The present chemical notation is due to Berzelius (1811), who replaced Dalton's inconvenient circular symbols by the initial letter, or, in cases where the names of several elements had the same initial letter, the initial and one other letter, of the Latin name.

The **symbol** of an element has a quantitative significance, and represents one **atom,** or one **atomic weight,** of the element. Thus, H represents 1 part by weight of hydrogen ; O represents 15·88 parts by weight of oxygen ; Cl represents 35·2 parts by weight of chlorine, and so on. This is the most important feature of the system of chemical notation.

The symbols of the elements, with their atomic weights, are given in the table on p. 145. The following are the less obvious symbols with which the reader should make himself familiar :

ENGLISH NAME.	LATIN NAME.	SYMBOL	ATOMIC WEIGHT (approximate).
Antimony	*stibium*	Sb	120
copper	*cuprum*	Cu	63·5
mercury	*hydrargyrum*	Hg	200
silver	*argentum*	Ag	107
gold	*aurum*	Au	197
iron	*ferrum*	Fe	56
lead	*plumbum*	Pb	207
potassium	*kalium*	K	39
sodium	*natrium*	Na	23
tin	*stannum*	Sn	119

The symbol W is given to tungsten, from the German name *wolfram.* These symbols of the elements are the same in all languages, with the exception of Az (*azote*), sometimes used in French for nitrogen. The names *glucinum* (Gl) and *columbium* (Cb) are sometimes used for beryllium and niobium, respectively, from the Greek *glukos*, sweet-tasting, and Columbia (America).

The names of compounds.—The names of compounds are formed from those of their constituents in such a way as to indicate their composition.

In the names of compounds of two elements, or **binary compounds,** the name of one element, the more electropositive (p. 275), comes first, followed by the name of the other element, suitably contracted and with the termination **-ide.** The order in which the elements are taken in forming the names is as follows :

Metals.
Carbon.
Hydrogen.
Nitrogen, phosphorus, arsenic.
Sulphur, selenium, tellurium.
Halogens (fluorine, chlorine, bromine, iodine).
Oxygen.

E.g., 2 atoms of hydrogen + 1 atom of sulphur form hydrogen sulphide, H_2S.
1 atom of sodium + 1 atom of chlorine form sodium chloride, $NaCl$.
1 atom of calcium + 2 atoms of carbon form calcium carbide, CaC_2.
2 atoms of sulphur + 2 atoms of chlorine form sulphur chloride, S_2Cl_2.
2 atoms of chlorine + 1 atom of oxygen form chlorine monoxide, Cl_2O.

The formulæ of compounds.—These are made by writing the symbols of the elements together, with a small numerical suffix to indicate how many atoms of each element are present in a molecule of a compound, as shown in the table above. The number unity is always understood if no suffix is written.

Since two elements often combine in more than one proportion, giving different compounds, this is represented in the nomenclature in one of two ways : (1) by suffixes, (2) by prefixes.

Thus, the two oxides of copper are :

$$\left.\begin{array}{l}\text{Red oxide of copper, } Cu_2O\text{, cupr}\textbf{ous}\text{ oxide}\\ \text{Black oxide of copper, } CuO\text{, cupr}\textbf{ic}\text{ oxide}\end{array}\right\}\text{ Suffixes.}$$

Two oxides of sulphur are :

$$\left.\begin{array}{l}SO_2\text{, sulphur }\textbf{di}\text{oxide}\\ SO_3\text{, sulphur }\textbf{tri}\text{oxide}\end{array}\right\}\text{ Prefixes.}$$

The suffix **-ous** denotes the *lower*, the suffix **-ic** the *higher*, pro portion of an element. The suffixes are always added to the Latin names :—

Green chloride of iron, $FeCl_2$, ferr**ous** chloride, or iron **di**chloride.
Red chloride of iron, $FeCl_3$, ferr**ic** chloride, or iron **tri**chloride.

The prefixes **sub-, proto-,** and **sesqui-** have practically gone out of use :
Cu_2O, copper **sub**oxide, now called cupr**ous** oxide.
CuO, copper **prot**oxide, now called cupr**ic** oxide.
FeO, iron **prot**oxide, now called ferr**ous** oxide.
Fe_2O_3, iron **sesqui**oxide, now called ferr**ic** oxide.

In a series of oxides, the one containing the *highest* proportion of oxygen is often called a **peroxide :**

Lead **sub**oxide, Pb_2O.
Lead **mon**oxide, Litharge, PbO.
Lead **sesqui**oxide, Pb_2O_3.
Triplumb**ic tetr**oxide, Red lead or minium, Pb_3O_4.
Lead **per**oxide, Puce-coloured oxide of lead, PbO_2.

It has been proposed to restrict the term *peroxide* to a special class of oxides, viz., those giving hydrogen peroxide (H_2O_2) with acids, such as Na_2O_2, BaO_2. In this case PbO_2 would be called lead **di**oxide. The highest oxide of nitrogen definitely known is the **pent**oxide, N_2O_5, which is never called the peroxide, the latter name being very improperly used for the **di**oxide, NO_2—apparently because many true peroxides are dioxides (BaO_2, etc.). The name **peroxide** is, in fact, very loosely used, and causes great confusion to beginners ; it would seem desirable to use it only in the restricted sense just explained.

The common names, or special names, are frequently used for compounds instead of the systematic names. Thus : water (H_2O), ammonia (NH_3), hydrazine (N_2H_4), hydrazoic acid (HN_3), sulphuretted hydrogen (H_2S).

Acids, bases, and salts.—Compounds of **three** elements are called **ternary compounds ;** the most important belong to the classes known as **acids, bases,** and **salts,** containing oxygen. The terminations **-ous** and **-ic** are then used to distinguish **acids** containing less and more oxygen, the terminations **-ite** and **-ate** being used for the corresponding **salts :**

Acid.	**Salt.**
Sulphur**ous**, H_2SO_3	Sodium sulph**ite**, Na_2SO_3
Sulphur**ic**, H_2SO_4	Cupric sulph**ate**, $CuSO_4$
Nitr**ous**, HNO_2	Potassium nitr**ite**, KNO_2
Nitr**ic**, HNO_3	Lead nitr**ate**, $Pb(NO_3)_2$

If more than two oxy-acids of an element exist, the prefixes **hypo-** (*below*) and **per-** (*above*) are used :

Hyposulphur**ous** acid, $H_2S_2O_4$	Sodium **hypo**sulph**ite**, $Na_2S_2O_4$
Sulphur**ous** acid, H_2SO_3	Potassium sulph**ite**, K_2SO_3
Sulphur**ic** acid, H_2SO_4	Lead sulph**ate**, $PbSO_4$
Persulphur**ic** acid, $H_2S_2O_8$	Potassium **per**sulph**ate**, $K_2S_2O_8$.

Oxides yielding acids with water are called **acidic oxides,** or **acid anhydrides** (*α without* ; *ὕδωρ* (*hudor*) *water*) :

SO_2, sulphur**ous** anhydride	SO_3, sulphur**ic** anhydride
P_2O_3, phosphor**ous** anhydride ;	P_2O_5, phosphor**ic** anhydride
N_2O_3, nitr**ous** anhydride ;	N_2O_5, nitr**ic** anhydride

Oxides yielding **bases** (alkalies or alkaline earths) with water are called **basic oxides ;** they formerly often had names ending in **-a,** some of which are still used :

Na_2O, soda ;
(K_2O, potash) ;
Li_2O, lithia ;
(CaO, lime)
MgO, magnesia
BaO, baryta.

By the combination of basic oxides with water, **bases** are produced. These contain a metal (or radical, *cf.* below) united with a group of atoms OH, called **hydroxyl,** and they are therefore called **hydroxides** (not " hydrates "). Hydroxides of sodium, potassium, and other so-called alkali-metals are called **alkalies ;** those of calcium, strontium, and barium are called **alkaline earths.**

$K_2O + H_2O = 2KOH$ (**potassium hydroxide ;** *caustic potash*).
$CaO + 2H_2O = Ca(OH)_2$ (**calcium hydroxide,** *slaked lime*).

By the combination of acidic oxides with water, **acids** are produced : $SO_3 + H_2O = H_2SO_4$ (sulphuric acid).

Acidic and basic oxides combine to form **salts :**

$$SO_3 + Na_2O = Na_2SO_4 \text{ (sodium sulphate).}$$

Acids and bases also interact to produce salts, but water is at the same time eliminated :

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

The salt Na_2SO_4 may be regarded as sulphuric acid in which two atoms of hydrogen are replaced by two atoms of sodium. Thus, acids may be considered as **salts of hydrogen,** which hydrogen can be displaced by metals. This takes place directly, for instance, when metallic zinc dissolves in dilute sulphuric acid :

$$Zn + H_2SO_4 = ZnSO_4 \text{ (zinc sulphate)} + H_2.$$

Salts are also formed by the action of acids on basic oxides, or carbonates; in the second case gaseous carbon dioxide is evolved with effervescence:

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$
$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Radicals.—In certain compounds a **group of atoms** plays the part of a single atom, and occurs in a whole series of combinations with other atoms. Thus the salts formed by the combination of ammonia, NH_3, with acids all contain the group NH_4, which plays the part of a metal, and is called **ammonium**:

$NH_3 + HCl = NH_4Cl$, **ammonium chloride** (*cf.* potassium chloride, KCl).

$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$, **ammonium sulphate** (*cf.* potassium sulphate, K_2SO_4).

Such an unvarying group of atoms present in a series of closely related compounds is called a **radical** (Latin, *radix*, a root). The group OH (hydroxyl) in bases is a radical.

Chemical calculations.—The systematic notation of chemistry leads to a great simplification of numerical calculations. The symbol of an element represents one atom, *i.e.*, a definite weight, and the formula of a compound represents one molecule, the weight of which is the sum of the weights of the atoms contained in it. Calculations of chemically interacting weights are then reduced to simple proportions.

The notation is also applicable to the representation of the interaction of elements and compounds; the resulting expressions are called **chemical equations**, and have a quantitative significance.

The formula of a compound is easily found from its percentage composition, and *vice versa*. The simplest possible formula derived from the percentage composition is called the **empirical formula.**

To find the formula from the percentage composition we divide the percentage of each element by its atomic weight and obtain a series of numbers in proportion to the numbers of atoms of the elements in the molecule of the compound. This series, reduced to the ratios of the smallest *whole* numbers, will give us the empirical formula.

The slight differences from whole numbers often found are due to experimental errors in the percentage composition. This process of rounding off must be used with caution: the empirical formula of cane-sugar is $C_{12}H_{22}O_{11}$, which might be written CH_2O, and the difference put down to experimental errors, if there was not other evidence that $C_{12}H_{22}O_{11}$ is the correct formula.

Since the symbols denote atomic and molecular weights, the same number of atoms of the same elements must occur (in different groupings, it is true) on each side of a chemical equation ; or, as is said, **the equation must balance.**

SUMMARY OF CHAPTER VIII

The laws of stoichiometry are explained by a **hypothesis** called the **atomic theory.** This supposes that: (1) all matter is made up of minute particles, called **atoms,** which are undivided in chemical changes ; (2) the atoms of each element are identical ; (3) in chemical combination a whole number of atoms of one element is associated with a whole number of atoms of another element, or elements, to form a **molecule** of the compound.

Each atom has a definite, but exceedingly small, weight or mass. The **absolute mass** of the lightest atom, viz., that of hydrogen, is $1{\cdot}66 \times 10^{-24}$ gm. The ratio of the weight of an atom of any element to the weight of the hydrogen atom is called the **atomic weight** of the element. Each element has a **symbol,** denoting one atomic weight of the element. The **formula** of a compound, denoting one molecular weight, contains the symbols of its constituent elements written side by side, each with a numerical suffix indicating how many atoms of that element occur in the molecule of the compound.

EXERCISES ON CHAPTER VIII

1. Explain what is meant by a *hypothesis*. Give a short account of the origin and content of the atomic hypothesis used in chemistry. Mention any other hypotheses with which you are acquainted.

2. From what sources are the names of the chemical elements derived ? How are they denoted by symbols ?

3. Describe carefully, with the use of an example, what are the separate steps involved in a chemical calculation. On what experimental and theoretical results are these steps based ?

4. Barium peroxide has the formula BaO_2. On heating, it evolves oxygen gas, with the formula O_2, and leaves a residue of baryta, BaO. Write the chemical equation of the reaction, and, from the result that 31·76 gm. of oxygen at S.T.P. occupy 22·3 litres, find the weight of barium peroxide required to make 10 litres of oxygen, measured at 15° and 740 mm.

5. Potassium dichromate has the formula $K_2Cr_2O_7$. On heating with concentrated sulphuric acid it gives off oxygen gas and water vapour, and leaves a residue containing potassium sulphate, K_2SO_4, and chromium sulphate, $Cr_2(SO_4)_3$. Write down the equation of the reaction, and find how many litres of oxygen, measured at 10° and 762 mm., are evolved from 1 kgm. of dichromate.

6. What weights of crystallised potassium ferrocyanide and of concentrated sulphuric acid, sp. gr. 1·84, are required to prepare 100 gr. of carbon monoxide (p. 702) ? Sulphuric acid of sp. gr. 1·84 contains 96·6 per cent. H_2SO_4.

CHAPTER IX

AVOGADRO'S HYPOTHESIS AND THE MOLECULE

The law of gaseous volumes.—Reference has been made to the determination of the relative combining volumes of hydrogen and oxygen, which were found by Cavendish to be very nearly 2 : 1. Alexander von Humboldt and Joseph Louis Gay-Lussac in 1805 confirmed this result, and the latter, impressed by the simplicity of the ratio, extended the researches to other chemical reactions between gases. In 1808 he published the results, and from them deduced the following law: **When chemical changes occur between gases, there is always a simple relation between the volumes of the interacting gases, and also of the products, if these are gaseous.** The same conditions of temperature and pressure are assumed.

Examples.

1 volume of oxygen combines with 2 volumes of hydrogen to give 2 volumes of steam.

1 volume of chlorine combines with 1 volume of hydrogen to give 2 volumes of hydrochloric acid.

2 volumes of carbonic oxide combine with 1 volume of oxygen to give 2 volumes of carbonic acid.

2 volumes of nitrogen combine with 1 volume of oxygen to give 2 volumes of nitrous oxide.

1 volume of nitrogen combines with 1 volume of oxygen to give 2 volumes of nitric oxide.

1 volume of nitrogen combines with 2 volumes of oxygen to give 2 volumes of nitrogen dioxide.

1 volume of nitrogen combines with 3 volumes of hydrogen to give 2 volumes of ammonia.

Later experiments (p. 213) show that the law is not quite exact. Burt and Edgar found the combining volumes of hydrogen and oxygen to be 2·00288 : 1; Gray and Burt from 2 volumes of hydrochloric acid gas obtained 1·0079 volumes of hydrogen;

Guye and Pintza showed that 1 volume of nitrogen combines with 3·00172 volumes of hydrogen to form ammonia. All these numbers refer to S.T.P. The slight differences from whole numbers appear to be due to the different compressibilities of the gases, *i.e.*, the deviations of the gases from Boyle's law.

Thus, if 100 c.c. of oxygen at S.T.P. are converted into carbon dioxide by burning carbon in the gas, the volume is found to have contracted slightly. Carbon dioxide is more compressible than oxygen, and occupies a slightly smaller volume than that of the oxygen it contains.

Gay-Lussac remarked that, since gases combine by weight in atomic proportions, or simple multiples of these, and by volume in simple ratios, there must be some simple relation between the atomic weights and the combining volumes. Berzelius made the assumption that equal volumes of elementary gases contain equal numbers of atoms. Dalton objected strongly to this statement. In the first place, his own (inexact) measurements of combining volumes did not confirm Gay-Lussac's law : thus, he found that 1·97 volumes of hydrogen combine with 1 volume of oxygen. In the second place, he pointed out that the density of a gas is not the same thing as the weight of its ultimate particle ; steam, for instance, is lighter than oxgyen, whereas the ultimate particle of steam must be heavier than that of oxygen, since it contains the latter.

A more serious difficulty was also pointed out by Dalton. One volume of oxygen combines with 1 volume of nitrogen to produce 2 volumes of nitric oxide. Now if 1 volume of oxygen (say 1 litre) contains n atoms, then 1 litre of nitrogen will also contain n atoms. Combination occurs between equal volumes, therefore, according to the above theory, atom for atom ; hence there will be n molecules of nitric oxide produced. But these are found to occupy a volume of 2 litres, hence nitric oxide can contain only half as many particles in a given volume as nitrogen or oxygen. Avogadro in 1811 set out to explain this discrepancy, and he succeeded in clearing away all the difficulties by a simple assumption which, when it was made, appeared almost obvious.

Avogadro's Hypothesis.—Avogadro began by assuming that the simple hypothesis of equal numbers of particles in equal volumes is correct. The discrepancies must then arise from an incorrect method of applying the hypothesis to the experimental results.

Avogadro's hypothesis, that **equal volumes of all gases and vapours, under the same conditions of temperature and pressure, contain identical numbers of molecules,** shows that " the ratios of the masses of the molecules are the same as those of the densities of the different gases at equal temperature and pressure."

By a **molecule** is meant **the smallest mass of a substance capable of existing in the free state.**

In the case of **gases** we shall see (Chapter XV) that the molecules are in motion, and Maxwell has defined a molecule as *that small portion of matter which moves about as a whole so that its parts, if it has any, do not part company during the motion of agitation of the gas.* There is reason to believe that the constitution of **liquids** is similar to that of gases, but the molecules are closer together and glide over one another. In **solids,** the molecules probably perform small oscillations about stationary positions (p. 271).

Molecules of gases.—The difficulty which had confronted Gay-Lussac and Berzelius was now cleared away. Avogadro pointed out that *the molecules of elementary gases are not necessarily the atoms themselves, but usually consist of groups or clusters of atoms, moving about as though they were single particles.* Both kinds of particles, atoms and molecules, had been called " atoms " by Dalton, but they were really different. Avogadro arrived at this important conclusion as follows.

Chlorine and hydrogen combine in equal volumes to form a volume of hydrochloric acid equal to the sum of the volumes of the elementary gases. Equal volumes of chlorine and hydrogen, however, contain identical numbers of molecules, say n. The 2 volumes of uncombined mixed gases will therefore contain $2\ n$ molecules, of which n are of hydrogen, and n are of chlorine. After combination, the 2 volumes of hydrochloric acid must by hypothesis also contain $2\ n$ molecules. Now each molecule of hydrochloric acid must contain at least one atom each of chlorine and hydrogen, hence there must be at least $2\ n$ atoms of each element present. Thus, the n molecules of chlorine gas, and the n molecules of hydrogen gas, must each have contained $2\ n$ atoms; in other words, a molecule of each of the elementary gases must contain *at least two* atoms.

Volume diagrams.—This reasoning is most clearly grasped by the use of **volume diagrams,** in which the volumes of the gases are represented by squares or rectangles, and the molecules by small circles. It must be emphasised that Avogadro's hypothesis does not assert that the volumes of the actual *molecules* themselves are equal, but only that the volumes of the *gases* which contain equal numbers of molecules are identical. The compressibility of gases, and the relatively small volumes to which they are reduced by liquefaction, show that there are large spaces between the molecules in a gas, and the different volumes of liquid obtained from equal volumes of different gases indicate that the actual molecules of different gases have different sizes. All the gases will be considered at the same temperature and pressure.

Example 1.—**Combination of hydrogen and oxygen** (Fig. 73).—2 volumes of hydrogen + 1 volume of oxygen = 2 volumes of steam.

∴ 2 *n* molecules of hydrogen + *n* molecules of oxygen = 2 *n* molecules of steam.

4 *n* atoms of hydrogen + 2 *n* atoms of oxygen = 2 *n* molecules of steam (containing 6 *n* atoms).

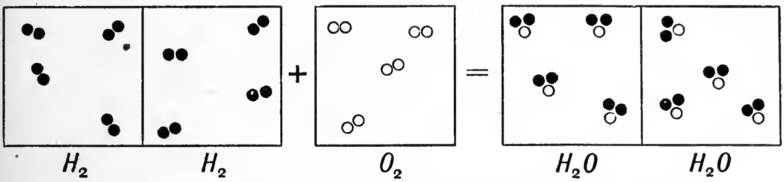


Fig. 73.—Diagram illustrating combination of Hydrogen and Oxygen.

Example 2.—**Combination of hydrogen and chlorine** (Fig. 74).—1 volume of hydrogen + 1 volume of chlorine = 2 volumes of hydrochloric acid.

∴ *n* molecules of hydrogen + *n* molecules of chlorine = 2 *n* molecules of hydrochloric acid.

2 *n* atoms of hydrogen + 2 *n* atoms of chlorine = 2 *n* molecules of hydrochloric acid (4 *n* atoms).

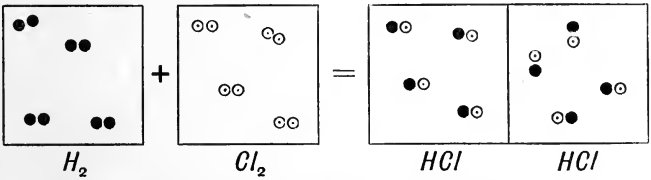


Fig. 74.—Diagram illustrating combination of Hydrogen and Chlorine.

Example 3.—**The combustion of carbon in oxygen to form carbon dioxide** (Fig. 75).—In this case we know nothing of the composition of the molecules of carbon, since these are present in a **solid**, to which Avogadro's hypothesis does not apply. If we **assume** that *one* atom of carbon combines with *two* atoms of oxygen to form a molecule of carbon dioxide, the fact that no change in volume occurs when carbon burns in oxygen is explained, but it is clear that the same result is obtained if we assume that *n* atoms of carbon combine with 2 atoms of oxygen to produce a molecule of carbon dioxide. The only result which may be deduced directly is that a molecule of carbon dioxide contains a molecule of oxygen (2 atoms).

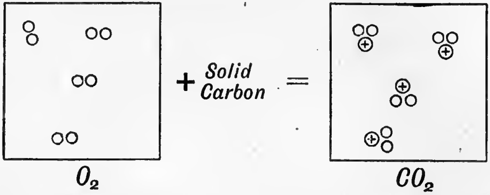


FIG. 75.—Diagram illustrating combination of Carbon and Oxygen.

Molecular weight and relative density.—The **molecular weights** of substances which exist in the gaseous state, or can be converted into vapours, may be compared by finding the ratio of the densities. The weight of any volume of the gas or vapour is compared with the weight of an equal volume of a standard gas under the same conditions :

$$\frac{\text{Mol. wt. of substance}}{\text{Mol. wt. of standard}} = \frac{\text{Wt. of any vol. of substance}}{\text{Wt. of equal vol. of standard}},$$

by Avogadro's hypothesis.

The molecular weight of a substance is defined as the sum of the atomic weights of its constituents :

$$\textbf{Molecular weight} = \frac{\text{Wt. of a molecule of substance}}{\text{Wt. of an } atom \text{ of hydrogen}}.$$

The relative density of a gas or vapour has been defined as :

$$\textbf{Relative density} = \frac{\text{Wt. of any vol. of gas or vapour}}{\text{Wt. of equal vol. of hydrogen}},$$

both substances being under the same conditions. But equal volumes contain equal numbers of molecules :

$$\therefore \quad \textbf{Relative density} = \frac{\text{Wt. of } n \text{ molecules of substance}}{\text{Wt. of } n \text{ molecules of hydrogen}}$$

$$= \frac{\text{Wt. of one molecule of substance}}{\text{Wt. of one molecule of hydrogen}}$$

$\therefore$ **Molecular weight = relative density × molecular weight of hydrogen.**

The molecular weight of hydrogen is defined in the same way as other molecular weights, viz., as the ratio of the weight of a molecule of hydrogen to that of an atom of hydrogen. Since gaseous compounds of hydrogen, when formed from hydrogen gas, may occupy double the volume of the latter, but never occupy more than double the volume, it may be assumed that the molecule of hydrogen consists of two atoms; in other words, the molecular weight of hydrogen is two. Thus:

Molecular weight = Relative density × 2.

Determination of atomic weight from gas or vapour densities.—Cannizzaro in 1858 showed that Avogadro's hypothesis can be systematically applied in the determination of **atomic weights.** By means of vapour density measurements, the molecular weights of as many volatile compounds of an element as possible are found. By analysis, it is then found what weights of the particular element are contained in the molecular weights of the various compounds. These must be whole multiples of the atomic weight, and, if the number of compounds taken is large enough, at least one of the weights of the element present in the molecular weights of its compounds will probably be the atomic weight itself.

The atomic weight of an element is the least weight of the element contained in a molecular weight of any of its compounds.

It will be seen that this is not an independent definition of atomic weight, but is merely a consequence of the molecular theory.

It cannot be too strongly emphasised that the determination of the relative density of one compound of an element, or of the element itself if it is volatile, can give no sure indication of the atomic weight. The molecules of the particular compound selected, and those of the vapour of the free element, may contain two, three, or any number of atoms of the element, for all we know to the contrary. The larger the number of compounds investigated, the greater is the probability that at least one contains only one atom of the element in a molecule.

The method used by Cannizzaro may be illustrated by a table of oxygen compounds. The numbers are approximate only.

OXYGEN COMPOUNDS.

Compound.	**Rel. density** (H = 1) Δ	**Mol. wt.** = 2 × Δ	**Wt. of oxygen in one mol. wt. of compound.**
Oxygen gas	16	32	16
Water	9	18	16
Carbon monoxide	14	28	16
Carbon dioxide	22	44	16 × 2
Sulphur dioxide	32	64	16 × 2
Sulphur trioxide	40	80	16 × 3
Alcohol	23	46	16
Ether	37	74	16
Nitrous oxide	22	44	16
Nitric oxide	15	30	16

The least weight of oxygen found in a molecular weight of any one of these compounds is 16, and hence this must be taken as the atomic weight.

A molecule of water contains one atom of oxygen, of weight 16, and therefore contains 18 — 16 = 2 parts, or two atoms, of hydrogen. The formula of water is therefore H_2O. In this way the problem which had eluded Dalton, of finding the number of atoms of the elements in the molecule of a compound, is easily solved.

Similarly, a table of carbon compounds may be drawn up.

CARBON COMPOUNDS.

Compound.	**Rel. density** (H = 1) Δ	**Mol. wt.** $= 2 \times \Delta$	**Wt. of carbon in one mol. wt. of compound.**
Methane	8	16	12
Ethane	15	30	12×2
Ethylene	14	28	12×2
Alcohol	23	46	12×2
Ether	37	74	12×4
Benzene	39	78	12×6
Carbon monoxide	14	28	12
Carbon dioxide	22	44	12

The atomic weight of carbon deduced from these results is 12. Thus, in 78 parts of benzene there are 72 parts, or 6 atoms, of carbon. Hence there are 78 — 72 = 6 parts, or 6 atoms, of hydrogen. The formula of benzene is thus C_6H_6.

The molecular weights found from the relative densities are only approximate, since the vapours do not accurately obey the gas laws, and the determinations are usually made only roughly. The accurate values of the atomic and molecular weights are found from the refined chemical analyses of the compounds, and the vapour density measurements used simply to decide between various possible molecular weights (see p. 147).

By drawing up tables similar to the above for as many elements as possible, we arrive at the atomic weights of these elements. In some cases, an element does not form volatile compounds, so that the method cannot be applied. Alternative methods must then be used, which are described in the next section.

Confirmation of atomic weights.—The atomic weights derived from the relative densities have been confirmed by a variety of independent methods. These remove the possibility that the least weight of an element found in the molecular weights of all the compounds examined may still be a multiple of the atomic weight, since it is very improbable that *all* the independent methods

INTERNATIONAL ATOMIC WEIGHTS (1921).

Element.	Symbol.	Atomic weight.	
		H = 1	O = 16
Aluminium	Al	26·8	27·1
Antimony	Sb	119·2	120·2
Argon	A	39·6	39·9
Arsenic	As	74·37	74·96
Barium	Ba	136·28	137·37
Beryllium	Be	9·0	9·1
Bismuth	Bi	206·4	208·0
Boron	B	10·8	10·9
Bromine	Br	79·29	79·92
Cadmium	Cd	111·51	112·40
Cæsium	Cs	131·76	132·81
Calcium	Ca	39·75	40·07
Carbon	C	11·910	12·005
Cerium	Ce	139·15	140·25
Chlorine	Cl	35·18	35·46
Chromium	Cr	51·6	52·0
Cobalt	Co	58·50	58·97
Copper	Cu	63·07	63·57
Dysprosium	Dy	161·2	162·5
Erbium	Er	166·4	167·7
Europium	Eu	150·8	152·0
Fluorine	F	18·9	19·0
Gadolinium	Gd	156·1	157·3
Gallium	Ga	69·5	70·1
Germanium	Ge	71·9	72·5
Gold	Au	195·6	197·2
Helium	He	3·97	4·00
Holmium	Ho	162·2	163·5
Hydrogen	H	1·000	1·008
Indium	In	113·9	114·8
Iodine	I	125·91	126·92
Iridium	Ir	191·6	193·1
Iron	Fe	55·40	55·84
Krypton	Kr	82·26	82·92
Lanthanum	La	137·9	139·0
Lead	Pb	205·55	207·20
Lithium	Li	6·89	6·94
Lutecium	Lu	173·6	175·0
Magnesium	Mg	24·13	24·32
Manganese	Mn	54·49	54·93
Mercury	Hg	199·0	200·6
Molybdenum	Mo	95·2	96·0
Neodymium	Nd	143·2	144·3
Neon	Ne	20·0	20·2
Nickel	Ni	58·21	58·68
Niobium	Nb	92·4	93·1
Niton	Nt	220·6	222·4
Nitrogen	N	13·897	14·008
Osmium	Os	189·4	190·9
Oxygen	O	15·87	16·00
Palladium	Pd	105·9	106·7
Phosphorus	P	30·79	31·04
Platinum	Pt	193·6	195·2
Potassium	K	38·79	39·10
Praseodymium	Pr	139·8	140·9
Radium	Ra	224·2	226·0
Rhodium	Rh	102·1	102·9
Rubidium	Rb	84·77	85·45
Ruthenium	Ru	100·9	101·7
Samarium	Sa	149·2	150·4
Scandium	Sc	44·7	45·1
Selenium	Se	78·6	79·2
Silicon	Si	28·1	28·3
Silver	Ag	107·04	107·88
Sodium	Na	22·82	23·00
Strontium	Sr	86·93	87·63
Sulphur	S	31·81	32·06
Tantalum	Ta	180·1	181·5
Tellurium	Te	126·5	127·5
Terbium	Tb	157·9	159·2
Thallium	Tl	202·4	204·0
Thorium	Th	230·31	232·15
Thulium	Tm	167·2	168·5
Tin	Sn	117·8	118·7
Titanium	Ti	47·72	48·1
Tungsten	W	182·5	184·0
Uranium	U	236·3	238·2
Vanadium	V	50·6	51·0
Xenon	Xe	129·2	130·2
Ytterbium	Yb	172·1	173·5
Yttrium	Yt	88·62	89·33
Zinc	Zn	64·85	65·37
Zirconium	Zr	89·9	90·6

should agree with this particular multiple. These methods will be considered in more detail later; a brief summary only is given here.

1. The **ratio of the specific heats of a gas** or vapour at constant pressure, c_p, and at constant volume, c_v, respectively, viz., c_p/c_v, has, according to the kinetic theory (p. 598), the value 1·667 only when the molecule consists of a single atom. In 1875 Kundt and Warburg found that c_p/c_v had the value 1·667 for mercury vapour, hence the molecules of the latter consist of single atoms. The relative density of mercury vapour is 100, hence the molecular weight is 200. This, however, must in the present case be equal to the atomic weight. It was found, in fact, that 200 parts of mercury was the least weight ever contained in a molecular weight of the volatile compounds. If the atomic weight found by the latter method can be shown in one case, viz., mercury, to be the real atomic weight, and not a multiple, one may reasonably assume that in other cases also the method gives the real atomic weights.

2. Dulong and Petit in 1819 found that the product of the atomic weight and the **specific heat of a solid element** is approximately constant, and equal to 6·3. Hence if the specific heat of a solid element is determined, and 6·3 is divided by this number, we obtain an approximate value of the atomic weight. This may be used to check the value found by the vapour density method.

3. Mitscherlich in 1819 found that compounds having analogous formulæ crystallise in the same form, or are **isomorphous.** Thus, potassium chromate crystallises in the same form as potassium sulphate. The atomic weight of sulphur is found from the compositions and densities of its volatile compounds to be 32. The atomic weight of potassium is found from the specific heat to be 39. Thus the formula of potassium sulphate is found to be K_2SO_4. From its isomorphism with the sulphate we assume that the formula of the chromate is K_2CrO_4, and hence, from an analysis of the compound, we find the atomic weight of chromium to be 52. This is confirmed by the specific heat of the metal.

4. The **formulæ** of compounds which show undoubted similarities in chemical properties are usually similar. Thus, the oxides of iron, aluminium, and chromium are given the similar formulæ, Fe_2O_3, Al_2O_3, and Cr_2O_3. If the atomic weight of chromium is found, as above, those of aluminium and iron can readily be determined. This method is the least trustworthy of all. Thus, beryllium oxide is similar in practically all its chemical properties to aluminium oxide, but has the formula BeO.

5. The position of the element in the **Periodic system** (Chap. XXIV) is probably the most convincing proof that the present values of the atomic weights are the correct multiples. No other values would place the elements in their correct positions.

Molecular weights of elements.—It has been emphasised that the relative density of an element itself gives no indication of the value of the atomic weight. Molecules of elements in the gaseous state may contain from one to eight atoms :

Monatomic : Hg, Na, K, Zn, Cd, He, A, Ne, Kr, Xe, Nt, I, Cl(?), Bi.
Diatomic : H_2, O_2, N_2, Cl_2, Br_2, I_2, F_2, S_2, Se_2, Te_2, As_2, Sb_2(?), Bi_2.
Triatomic : O_3.
Tetratomic : P_4, As_4.
Hexatomic : S_6 (?).
Octatomic : S_8.
The absence of the types X_5 and X_7 is noteworthy.

Limiting densities.—A comparison of the **normal densities** of gases cannot give exact ratios of the molecular weights, even when the most accurate values of the densities are used. For, even if equal volumes of different gases contained accurately equal numbers of molecules at one particular pressure, these volumes would, on account of the slightly different compressibilities of the different gases, not remain exactly equal at another pressure. The numbers of molecules in these unequal volumes would, however, still be equal.

The unequal compressibilities of gases result from the deviations from Boyle's law, since the latter gives equal compressibilities for all gases. Since the deviation from Boyle's law becomes less and less as the pressure becomes smaller, and appears to vanish at very small pressures, it may be assumed that the ratio of the densities at very low pressure, or the ratio of the **limiting densities** ($p \rightarrow 0$), will give the exact ratio of the molecular weights (D. Berthelot, 1899).

If a mass W gm. of gas occupies at 0° a volume v litres under a pressure p atm., we may call the quotient W/pv the **density per unit pressure.** If the gas obeyed Boyle's law, this would be the same at all pressures, since then $pv = \text{const.}$ Owing to deviations from Boyle's law, the quotient depends on the pressure. If $p = 1$, we have the **normal density** ; if $p \rightarrow 0$ the quotient approaches the value for an ideal gas, which is called the **limiting density.** The ratio of the limiting densities of two gases is the ratio of the molecular weights :

$$M_a : M_b = \frac{W_a}{(p_0v_0)_a} : \frac{W_b}{(p_0v_0)_b},$$

where p_0v_0 is the limiting value of pv as $p \rightarrow 0$.

If D is the normal density of a gas, $D = \frac{W}{p_1v_1}$, where p_1v_1 is the value of pv for $p = 1$,

$$\therefore \textbf{limiting density} = \textbf{normal density} \times \left(\frac{p_1v_1}{p_0v_0}\right).$$

The ratio p_1v_1/p_0v_0 may be determined for any arbitrary mass of gas by two methods:

(i) For gases which deviate only slightly from Boyle's law between zero pressure and 1 atm., $(p_0v_0 - pv)/p_0v_0$, or the relative deviation from Boyle's law, may be assumed to be proportional to the pressure: $(p_0v_0 - pv)/p \times p_0v_0 = \text{const.} = A$. This is called the **compressibility coefficient.** Its value may be found from two measurements of pv between 1 atm. and zero pressure. Thus, $p_1v_1 = p_0v_0(1 - A)$, since $p_1 = 1$, *i.e.*, **limiting density** $\doteq \dfrac{\text{normal density}}{1 - A}$.

(ii) From a number of measurements of pv, a curve can be drawn in which pv is plotted against p. Extrapolation to $p = 0$ gives the value of p_0v_0, and then the limiting density is found by multiplying the normal density by $\left(\dfrac{p_1v_1}{p_0v_0}\right)$.

EXAMPLE 1.—The atomic weight of **oxygen** from the relative density.

	Normal density.	**Compressibility** $= A = 1 - p_1v_1/p_0v_0$
Hydrogen	0·089873	+ 0·00054
Oxygen	1·42906	− 0·000964

$$\text{Limiting density of hydrogen} = 0{\cdot}089873 \times \frac{1}{1 - 0{\cdot}00054} = 0{\cdot}089922 \text{ gm./lit.}$$

$$\text{Limiting density of oxygen} = 1{\cdot}42906 \times \frac{1}{1 + 0{\cdot}000964} = 1{\cdot}42768 \text{ gm./lit.}$$

The ratio of the limiting densities is equal to the ratio of the molecular, or in this case the atomic, weights; hence:

Atomic weight of oxygen = 1·42768/0·089922 = 15·877.

The number found by direct synthesis of water (p. 64) is 15·879.

EXAMPLE 2.—The atomic weight of **chlorine** from the density of hydrochloric acid (Gray and Burt).

	Normal density.	p_1v_1	p_0v_0	
Hydrogen chloride	1·63915	58403	55213	(extrapolated).

Limiting density of HCl = 1·63915 × 54803/55213 = 1·62698,
Molecular weight of HCl = 2 × 1·62698/0·089922 = 36·187,
Atomic weight of Cl = 36·187 − 1 = 35·187.

The value found by Edgar by direct synthesis of HCl is 35·186.

By heating aluminium in 2 volumes of hydrogen chloride, measured at S.T.P., 1·00790 volumes of hydrogen were obtained. The molecular weight of HCl is therefore:

$$\frac{1{\cdot}63915}{0{\cdot}089873} \times \frac{2}{1{\cdot}00790} = 36{\cdot}191,$$

agreeing to about 1 part in 10,000 with the value from the limiting density.

These examples show that the method of limiting densities gives results at least as accurate as those found by chemical methods. In some cases, greater accuracy is probably attained by the density method.

Gram-molecular volume.—The molecular weight in grams of any substance is called the **gram-molecular weight**, or sometimes the **mol.** In the case of gases, Avogadro's hypothesis shows that, at a given temperature and pressure, the gram-molecular weight will occupy a constant volume. At S.T.P. (0° and 760 mm.) this is called the **gram-molecular volume,** or sometimes the **molar volume.**

This value is the same for all gases only if the latter are in the ideal state : it may be calculated with close approximation from the *normal* density of hydrogen :

Gram-molecular volume=volume of 2 grams of hydrogen at S.T.P.

$$= \frac{2}{\text{normal density}} = \frac{2}{0{\cdot}089873} = 22{\cdot}25 \text{ litres.}$$

The *accurate* value, for an ideal gas, is obtained from the *limiting* density of hydrogen :

$$\textbf{Gram-molecular volume} = \frac{2}{0{\cdot}089922} = \mathbf{22{\cdot}242\ litres.}$$

In this book the value **22·24 litres** (H = 1) will be adopted.

The gas constant.—The general equation for an ideal gas is : pv/T = constant. For a gram-molecular weight of an ideal gas at S.T.P. : $p = 1$ atm., $v = 22{\cdot}24$ litres, $T = 273{\cdot}09$ ∴ the value of the constant in the above equation is $22{\cdot}24/273{\cdot}09 = \mathbf{0{\cdot}08145}$. This number, which is the same for a gram-molecular weight of *any* gas in the ideal state, is called the **gas constant**, and is denoted by R. Thus, the **general gas equation,** for a gm. mol. of an ideal gas, is $pv/T = R$, or $pv = RT$, where $R = 0{\cdot}08145$ if p is in atm., v in litres, and T is the absolute temperature Centigrade.

The value of R in **absolute units** may be calculated as follows : $p = 1$ atm. $= 1{\cdot}01313 \times 10^7$ dynes per sq. cm. ; $v = 22{\cdot}242$ litres $=$ 22242 c.c. ; $T = 273{\cdot}09°$. ∴ $R = \mathbf{8{\cdot}252 \times 10^7}$ **ergs per 1°.** In **heat units,** the value of R is obtained by dividing the value in ergs per degree by the mechanical equivalent of heat. $J = 4{\cdot}186 \times 10^7$ ergs per gram calorie, ∴ $R/J = \mathbf{1{\cdot}971}$ **gm. cal. per 1°.**

The volume occupied by n gm. mol. of a gas is n times that occupied by one gm. mol. under the same conditions. Thus, if V is the volume of n gm. mol. of gas, the general equation becomes $pV = n\,RT$. If the weight of the gas is W gm., and the molecular weight is M, $n = W/M$.

In calculations involving gaseous volumes, one may use either the general gas equation, $pv = nRT$, or, more conveniently, the relation that 1 gm. mol. at S.T.P. occupies 22·24 litres. The equations must be written so as to express reactions between molecules of the substances, since only in this case are the volume relations correctly given.

Thus, the equation $H + Cl = HCl$, although it gives the correct weight ratios, does not give the correct volume ratio. This is expressed by the molecular equation: $H_2 + Cl_2 = 2HCl$.

If solids or liquids participate in the reaction, their volumes are neglected, since Avogadro's law does not apply to them.

Example 1.—Find the volume of 100 gm. of chlorine at 15° and 5·4 atm. pressure.

(*a*) *From the gas equation*: $pv = nRT$.

$p = 5{\cdot}4$ atm.; $T = 273 + 15 = 288$; $R = 0{\cdot}08145$ lit. atm./degree; $n = 100/70{\cdot}4$;

$$\text{thus } v = \frac{0{\cdot}08145 \times 100 \times 288}{5{\cdot}4 \times 70{\cdot}4} = \mathbf{6{\cdot}17\ litres.}$$

(*b*) *From the molecular volume*:

1 gm. mol., or 70·4 gm., of chlorine occupies 22·24 litres at S.T.P.

100 gm. of chlorine = 100/70·4 gm. mol., and at 15° and 5·4 atm. this will occupy:

$$\frac{100 \times 22{\cdot}24 \times 288 \times 1}{70{\cdot}4 \times 273 \times 5{\cdot}4} = \mathbf{6{\cdot}17\ litres.}$$

In both cases the number is approximate, since chlorine departs considerably from the ideal state under the given conditions.

Abnormal vapour densities.—**Acetic acid** has the empirical formula CH_2O, and its vapour density at 250° under 760 mm. pressure is 29 ($H = 1$), hence the molecular weight is of the order of 58. But $C_2H_4O_2 = 60$, hence under these conditions the vapour has this formula. At lower temperatures, under 760 mm. pressure, the density is greater—*e.g.*, at 125° it is 44·5, corresponding with a molecular weight of 89, which approximates to $C_3H_6O_3 = 90$. The density also increases with the pressure when the temperature is constant, and the change with temperature or pressure occurs *gradually*, so that it is only at isolated points that the density corresponds with a chemical formula.

Playfair and Wanklyn (1862) pointed out that this apparent exception to Avogadro's law could be explained on the assumption that the vapour of acetic acid below 250° was a mixture of the normal molecules, $C_2H_4O_2$, with molecules of greater density, $C_3H_6O_3$ or $C_4H_8O_4$. The substance is then said to be **associated.** By rise of temperature, or decrease of pressure, the associated molecules *gradually* break up into the normal molecules: $(C_2H_4O_2)_2 \rightleftharpoons 2C_2H_4O_2$. It is probable that these associated molecules exist in the liquid acid.

A different behaviour is shown by another group of substances, of which **ammonium chloride** is typical. This salt is produced by the direct union of ammonia, NH_3, with hydrochloric acid, HCl, and its simplest formula is thus NH_3,HCl, or $NH_4Cl = 53{\cdot}2$. Bineau, however, found its vapour density to be only 12·4, giving a molecular weight of 24·8. This is roughly half the least possible theoretical value, and corresponds with the formula $N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}$. This and similar deviations (phosphorus pentachloride, ammonium carbamate, etc.) led Deville to question the validity of Avogadro's law, but the true explanation was put forward simultaneously and independently by Kopp, Kekulé, and Cannizzaro in 1857–8.

Dissociation by heat.—Mitscherlich in 1833 had observed that **antimony pentachloride** on volatilisation by heat breaks up partially into antimony trichloride and free chlorine: $SbCl_5 = SbCl_3 + Cl_2$. The two constituents recombine on cooling, but can be separated from the mixture by their different volatilities. Since the reaction is reversible, it may be written: $SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$. Reactions of this type are examples of **thermal dissociation,** *i.e.*, the gradual decomposition of a compound by heat, in such a way that the products of decomposition recombine on cooling. They differ from such reactions as the decomposition of potassium chlorate by heat, as the products of these remain uncombined even after cooling.

J. H. Gladstone (1849) also found that the pale yellow solid **phosphorus pentabromide** partially dissociates when heated into the vapour of the tribromide (colourless) and free bromine (red): $PBr_5 \rightleftharpoons PBr_3 + Br_2$. The vapour is red, owing to the presence of free bromine. If the vapour is contained in an open flask, bromine diffuses out, and the denser PBr_3 remains. It was therefore reasonable to assume that ammonium chloride also, on heating, breaks up into ammonia and hydrogen chloride: $NH_4Cl \rightleftharpoons NH_3 + HCl$, which recombine on cooling. The density would then, for complete decomposition, be half the theoretical density, because the decomposed gas occupies double the volume it would if no decomposition had taken place.

Pebal (1862) was able to confirm this assumption by separating the two gases, NH_3 and HCl, from the vapour by **diffusion.** Ammonia is much lighter than hydrochloric acid and therefore diffuses more rapidly (*cf.* p. 191).

Pebal used the apparatus shown in Fig. 76. The tube *D* contained a plug of asbestos, *c*, and above this was placed a piece of sal ammoniac (NH_4Cl), *d*. The tube was enclosed in a wide test-tube, contained in a jacket heated in a charcoal furnace. Hydrogen was passed in through the tubes *a*, *b*, on both sides of the plug, and escaped through tubes to *A* and *B*, containing pieces of blue and red litmus paper, respectively. The red litmus was turned blue, because ammonia escaped more rapidly through the asbestos plug than the hydrochloric acid; the latter was swept out through the other tube, and turned the litmus red. Deville objected to this experiment, on the ground that the vapour might have been decomposed by contact with the asbestos plug; Than (1864) then replaced the latter by a plug of solid sal ammoniac (Fig. 77) and obtained the same result, so that the **dissociation** of ammonium chloride was proved.

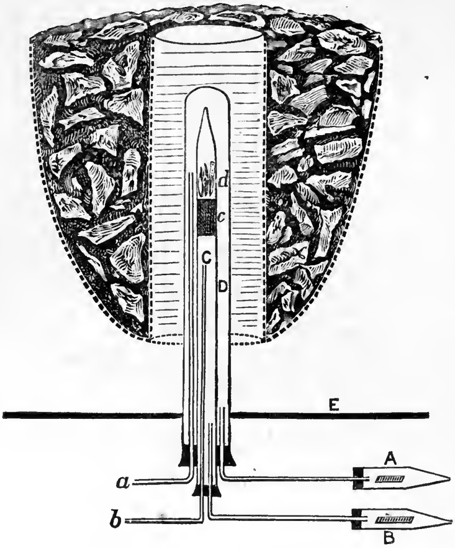


Fig. 76.—Pebal's Experiment on the Dissociation of Ammonium Chloride.

Marignac (1868) then showed that the absorption of heat required to volatilise ammonium chloride is practically equal to the heat evolved when the gases ammonia and hydrochloric acid combine together to produce the former compound, and hence the compound must split up into the two gases on volatilisation.

In dissociation, as in association, the change occurs gradually, so that a state of **chemical equilibrium** is established, in which the dissociating substance and the products of dissociation exist side by side: $NH_4Cl \rightleftharpoons NH_3 + HCl$. The extent of dissociation increases as the temperature rises, as is seen, for instance, in the progressive darkening in colour of the vapour of phosphorus pentabromide.

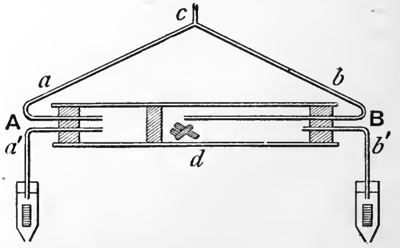


Fig. 77.—Than's Experiment on the Dissociation of Ammonium Chloride.

The dissociation of the colourless hydrogen iodide gas on heating may be seen from the violet colour of the iodine vapour produced:

$$2HI \rightleftharpoons H_2 + I_2.$$

Determination of the extent of dissociation from the vapour density.—The **degree of dissociation**, γ, *i.e.*, the fraction of the total number of molecules dissociated under given conditions, can in many cases be deduced from the **vapour density** of the substance. This method, however, is not applicable to cases where there is no change of volume on dissociation, *e.g.*, $HI + HI \rightleftharpoons H_2 + I_2$. In such cases the degree of dissociation must be determined by other methods (p. 348).

In the dissociation of substances such as phosphorus pentachloride, when a change of volume occurs:

$$\underset{\text{1 vol.}}{PCl_5} \rightleftharpoons \underset{\text{2 vols.}}{PCl_3 + Cl_2}$$

the progress of the dissociation may be followed by the vapour density.

Let each molecule of the initial substance break up into x molecules on dissociation. Then if γ is the degree of dissociation under given conditions, we shall have in the gas, if N molecules of substance are taken:

$N(1 - \gamma)$ molecules of original substance,

$Nx\gamma$ molecules of the products of dissociation.

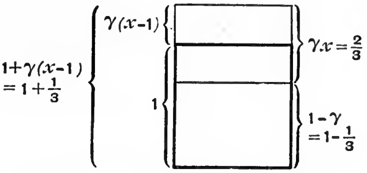


FIG. 78.—Diagram illustrating Dissociation.

The number of molecules before dissociation is N; that after dissociation is $N(1 - \gamma) + Nx\gamma = N[1 + \gamma(x - 1)]$ (see Fig. 78).

By Avogadro's law:

$$\frac{\text{Volume after dissociation}}{\text{Volume before dissociation}} = \frac{N[1 + \gamma(x - 1)]}{N}.$$

The **densities** are inversely proportional to the volumes. Let D be the normal vapour density, corresponding with the undissociated substance, Δ the observed vapour density, then:

$$D = \Delta[1 + \gamma(x - 1)]$$

$$\therefore \quad \gamma = \frac{D - \Delta}{\Delta(x - 1)}$$

If d is the vapour density corrresponding with complete dissociation, $d = D/x$.

In the case of phosphorus pentachloride, $x = 2$, hence:

$$\gamma = \frac{D - \Delta}{\Delta}.$$

Thus $d = \frac{1}{2}D$, *i.e.*, on complete dissociation the vapour density has half the normal value.

The dissociation of PCl_5 is easily demonstrated. Both PCl_5 and PCl_3 are colourless in the form of vapour; Cl_2 is greenish-yellow. The vapour of PCl_5, however, also shows a greenish-yellow colour, which becomes deeper as the temperature increases. At the same time the density (reduced to S.T.P.) decreases. Hence as the proportion of chlorine, or the extent of dissociation, increases, so the density decreases, under these conditions. The vapour also turns potassium iodide and starch paper blue, indicating the presence of chlorine.

At 200° and 1 atm. pressure, the vapour density of phosphorus pentachloride is 67·41. The density corresponding with no dissociation is $\frac{1}{2}PCl_5 = 100{\cdot}1$. Thus, $D = 100{\cdot}1$, $\Delta = 67{\cdot}41$. $\therefore\ \gamma = \frac{100{\cdot}1 - 67{\cdot}4}{67{\cdot}4} = 0{\cdot}485$. Thus, out of every 100 molecules of PCl_5 heated to 200° under 1 atm. pressure, 48·5 are dissociated into $PCl_3 + Cl_2$. The vapour densities and dissociations at various temperatures (1 atm. press.) are (Cahours, 1847):

t^0	182	190	200	230	250	274	288	300	336°
Δ	70·5	69·4	67·4	59·7	55·6	53·4	51·0	50·7	50·8
γ	0·417	0·443	0·485	0·674	0·800	0·875	0·962	0·973	0·970

If we plot γ and Δ against t, we obtain the **dissociation curves**, Fig. 79. These show three parts: two flatter end parts, near the limiting values of the densities corresponding with no dissociation and complete dissociation, respectively, and a rising or falling intermediate portion, where the influence of temperature is marked.

The mechanism of chemical reactions.—If the elements chlorine and hydrogen are brought together they react to form the compound hydrochloric acid; this is called **combination.** By suitable means (*e.g.*, electrolysis) it is possible to recover from hydrochloric acid, qualitatively and quantitatively, the elements of which it is composed, and the process is called **decomposition.**

Dalton regarded these changes as real combinations between atoms, and decompositions of compounds into atoms: $H + Cl = HCl$, and $HCl = H + Cl$, so that a nomenclature originally applied to substances was appropriate also to the atoms. With the advent of the molecular theory, this point of view could not be maintained. The reactions had then to be formulated as follows:

(1) $H_2 + Cl_2 = 2HCl$, or $HH + ClCl = HCl + HCl$, and
(2) $2HCl = H_2 + Cl_2$, or $HCl + HCl = HH + ClCl$.

They are now seen to be examples, not of simple combination and decomposition, but of **double decomposition,** *i.e.*, a special case of **rearrangement** of the atoms in different molecules, when the numbers of molecules before and after the reaction are the same.

In the same way, cases of **displacement** often lead to the elimination of molecules, not of atoms: $HgCl_2 + Zn = ZnCl_2 + Hg$ (atom); $Zn + 2HCl = ZnCl_2 + H_2$ (molecule).

Cases of true combination between atoms alone, or decomposition into atoms alone, are rare. Combination occurs between atoms and molecules, *e.g.*, $Hg + Cl_2 = HgCl_2$, or between molecules and molecules, *e.g.*, $CO + Cl_2 = COCl_2$, but is rarely observed between atoms alone: $I + I = I_2$. Many apparent cases of combination are really examples of double decomposition: $HH + II = HI + HI$. Again, a compound decomposes into molecules, *e.g.*, $CaCO_3 = CaO + CO_2$, or into molecules and atoms, *e.g.*, $2HgO = 2Hg + O_2$, but seldom into atoms alone. Other apparent cases of decomposition are really double decompositions: $HI + HI = HH + II$, or $2HI = H_2 + I_2$. **Double decomposition,** in fact, is the commonest type of chemical change.

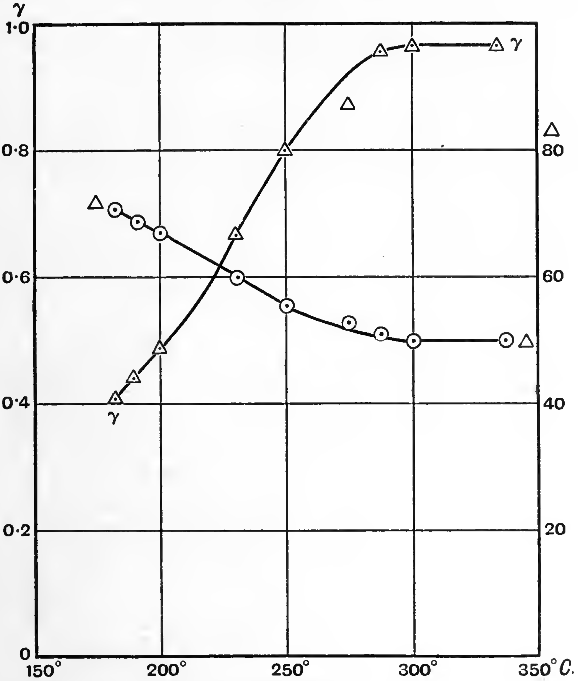


FIG. 79.—Dissociation Curves.

The **mechanism** of chemical changes then becomes much more complicated than on the basis of the atomic theory alone. Thus, the formation of water from gaseous oxygen and hydrogen, instead of being a simple combination: $2H + O = H_2O$, occurs between molecules, and possibly in stages, various types of which are possible:

1. Decomposition of the molecules into atoms, followed by simple

combinations between the latter: $H_2 = 2H$, $O_2 = 2O$, and $2H + O = H_2O$.

2. Direct combination between molecules, to form **hydrogen peroxide**, H_2O_2; $H_2 + O_2 = H_2O_2$, followed by
   (i): decomposition of the hydrogen peroxide by heat: $2H_2O_2 = 2H_2O + O_2$, or $H_2O_2 = H_2O + O$, followed by $H_2 + O = H_2O$; or, (ii): reduction of the hydrogen peroxide by another hydrogen molecule: $H_2O_2 + H_2 = 2H_2O$.

3. Double decomposition between hydrogen and oxygen molecules, to form a water molecule and an oxygen atom, the latter combining with another hydrogen molecule to form water: $H_2 + O_2 = H_2O + O$ and $H_2 + O = H_2O$.

Traube favoured scheme (2); Dixon's experiments led him to the opinion that scheme (3) is the most likely; scheme (1) has few supporters.

In the present state of chemistry it cannot be said with certainty which, if any, of these alternative groups of reactions really goes on in the combustion of hydrogen, or whether two or more of them proceed simultaneously. The case is no better with other simple reactions, and a large and intensely interesting field of inquiry still awaits investigation.

The case of **isomeric change** is also considerably amplified by the molecular theory. Two possibilities are obvious: (1) the different substances of the same empirical formula have the *same molecular weight*; they are then called **metamers,** and their interconversion, **metameric change**; or (2) they have *different molecular weights*, when those of higher molecular weight are called **polymers,** and their formation from the substance of lower molecular weight is called **polymerisation.**

SUMMARY OF CHAPTER IX

Gay-Lussac's law of volumes: *when chemical changes occur between gases, there is always a simple relation between the volumes of the interacting gases, and also of the products if these are gaseous.*

Avogadro's hypothesis: this explains Gay-Lussac's law, and states that: *equal volumes of all gases and vapours, under the same conditions of temperature and pressure, contain identical numbers of molecules.* It applies exactly to gases under very low pressures; under ordinary conditions it is only an approximate law.

A **molecule** *is the smallest portion of a substance which can exist in the free state.*

An **atom** of an element is *the smallest portion of it which can exist in a molecule of a compound.* In some cases (*e.g.*, Hg) the atom is identical with the molecule, but more usually the molecule consists of two or more atoms.

The **molecular weight** of a substance is *the ratio of the weight of a molecule of that substance to the weight of an* **atom** *of hydrogen.* It is twice the relative density of the gaseous or vapour form of the substance (H = 1), since the hydrogen molecule contains two atoms, H_2.

The molecular weight in grams of any gas (**gm. mol.**) occupies at S.T.P. a volume of 22·24 litres (**gm. mol. vol.**).

Many compounds on heating **dissociate,** *i.e.*, are partially decomposed, to an extent increasing with the temperature, in such a way that the products recombine on cooling. If change of density occurs, the **degree of dissociation,** *i.e.*, the fraction of the total number of molecules which are broken up, may be calculated from the equation: $\gamma = (D - \Delta)/\Delta(x - 1)$, where D = density of undissociated substance; Δ = observed density, both reduced to S.T.P., and x = number of molecules formed on dissociation from one molecule of the substance.

EXERCISES ON CHAPTER IX

1. State Gay-Lussac's law of volumes, and describe two experiments which could be performed to demonstrate its truth. Does the law hold accurately ? What explanation may be given for the deviations found by experiment ?

2. Describe the evidence which led Avogadro to assume that the smallest particles of gases usually consist of more than one atom. What reason is there for the assumption that the molecules of hydrogen, oxygen, and chlorine consist of two atoms, whilst that of mercury vapour consists of only one ?

3. What weight of barium peroxide must be decomposed by heating to give 42 litres of oxygen at 18° and 740 mm. ?

4. The molecular weight of cyanogen is 52·08 (O = 16). Find its density referred to air = 1, and its normal density. It contains 46·08 per cent. of carbon and 53·92 per cent. of nitrogen ; what is its formula ? What volumes of nitrogen and carbon monoxide would be formed by exploding 1 litre of cyanogen with oxygen ?

5. Explain why the atomic weights of carbon, oxygen, and sulphur are taken as 12, 16, and 32 instead of 6, 8, and 16, the values adopted by Gmelin.

6. The normal densities of chlorine, carbon dioxide, and ammonia are 3·220, 1·9768, and 0·7708 gm. per litre, respectively. Calculate the gram-molecular volumes (H = 1), and explain why these are not exactly equal to 22·24 litres.

7. Show that the molecular weight in *ounces* of a gas occupies nearly the same volume in *cubic feet* as the molecular weight in grams occupies in litres.

8. Calculate the atomic weights and molecular volumes of chlorine and hydrogen on the atomic weight standard O = 100.

9. Discuss the nature of chemical change from the point of view of the molecular theory. Criticise the statement: "hydrogen and oxygen combine to form water." In what sense is it correct ?

10. Explain, with examples, the methods used in deciding which multiple of the equivalent is the atomic weight of an element.

The chloride of an element contains 37·322 per cent. of chlorine. The vapour density of the chloride is 190 (H = 1). The specific heat of the element is 0·0276. Find the atomic weight of the element, and the formula of the chloride.

11. Describe the cases of abnormal vapour densities met with. What explanation of these has been given, and what evidence is there of its correctness ?

12. Define *dissociation*. In what way does it differ from such changes as the decomposition of potassium chlorate by heat ?

13. Using a porcelain Victor Meyer apparatus (p. 87) the following data were obtained for iodine : 0·0874 gm. of iodine displaced 13·7 c.c. of air. Barometer 722·8 mm. ; temperature of room 21·5° ; vapour pressure of water at 21·5° = 19·2 mm. Calculate the vapour density of iodine, and the degree of dissociation at the temperature of the experiment (I = 127).

14. Under what conditions is Avogadro's law strictly applicable ? Show how the molecular weight of a gas may be found accurately from the density. The weight of 1 litre of a gas at S.T.P. is 1·2507 gm. ; its compressibility coefficient is −0·000559. Find its molecular weight (H = 1).

CHAPTER X

OXYGEN. ($O = 15{\cdot}87$)

Occurrence of oxygen.—The element **oxygen** ($O = 15{\cdot}87$) occurs in the **free state** as a gas, of the molecular formula O_2. It is colourless, odourless, and tasteless, and supports combustion and respiration. It is the uncombined oxygen in the atmosphere, where it occurs to the extent of 21 per cent. by volume or 23 per cent. by weight, which takes part in processes of combustion ; its functions in respiration make it the most important element from the biological point of view. Oxygen is sparingly soluble in (and may therefore be collected over) water, but the small quantity of oxygen dissolved in river and sea waters is essential to the life of fish.

Combined oxygen occurs in water, in vegetable and animal tissues, and in nearly all minerals and rocks. Oxygen occurs to a larger extent in the earth's crust than any other element ; it makes up about 50 per cent. of the total quantity of the terrestrial elements.

Oxygen was first isolated by Scheele in 1772, and was discovered independently by Priestley in 1774 (p. 44).

According to Duckworth, the Chinese philosopher, Mao Khoá (eighth century) assumed two primary elements : *Yin* (the weak), and *Yang* (the strong). In air, yin and yang are combined with fire. When charcoal is burnt in air, yang is left, whilst yin could be obtained by heating a substance *Hhò-siaō* (possibly nitre). The Greek alchemist Zosimus (third century) also refers to a gaseous body evolved on heating a substance floating on the surface of heated mercury (possibly mercury oxide).

Preparation of oxygen.—Oxygen may be obtained by simply heating certain **metallic oxides,** viz., those of mercury, silver, gold, and the platinum metals.

If mercuric oxide is heated in a hard glass tube it decomposes ; globules of mercury collect in the cooler parts of the tube ; oxygen gas is evolved, and may be collected over water : $2HgO = 2Hg + O_2$ (Fig. 24). Oxide of silver, precipitated from silver nitrate solution by caustic potash (in absence of carbon dioxide), gives very pure oxygen when heated: $2Ag_2O = 4Ag + O_2$.

Oxygen is not evolved on heating the lower oxides of metals other than the above, but many **higher oxides,** including **peroxides** (p. 134), lose a portion of their oxygen at more or less elevated temperatures. Examples are **hydrogen peroxide,** H_2O_2; **barium peroxide** BaO_2; **lead dioxide,** PbO_2; **manganese dioxide,** MnO_2.

$2H_2O_2 = 2H_2O + O_2$; $2BaO_2 = 2BaO$ (baryta) $+ O_2$; $2PbO_2 = 2PbO + O_2$; $3MnO_2 = Mn_3O_4$ (trimanganic tetroxide) $+ O_2$.

Manganese dioxide (*pyrolusite*) is decomposed on heating to bright redness in an iron tube, and this reaction was formerly a cheap method of preparing oxygen on a moderate scale. The dioxide evolves oxygen at a lower temperature when heated with concentrated sulphuric acid in a glass flask: $2MnO_2 + 2H_2SO_4 = 2MnSO_4$ (manganous sulphate) $+ 2H_2O + O_2$: frothing, however, occurs, and dangerous explosions result if water is drawn back into the heated acid from the pneumatic trough. Lead dioxide loses oxygen fairly readily at a dull red heat, but the lead monoxide, or *litharge,* PbO, readily attacks glass or porcelain. None of these methods is now used.

Oxygen may be obtained from **water** by electrolysis (p. 56), or by removing the hydrogen with chlorine; the latter readily combines with hydrogen to form the stable hydrochloric acid, HCl, but does not unite directly with oxygen: $2H_2O + Cl_2 = 4HCl + O_2$.

EXPT. 61.—A stream of chlorine, generated from potassium permanganate and concentrated hydrochloric acid in a flask, is passed through water boiling in a second flask, and the gas is then passed through a silica tube packed with bits of broken porcelain and heated to bright redness in a furnace (Fig. 80). The gas is passed through caustic soda solution in a wash-bottle to remove excess of chlorine, and hydrochloric acid, and the oxygen is collected over water.

All modern processes for the preparation of oxygen in the laboratory make use of **salts rich in oxygen:** chlorates (*e.g.*, $KClO_3$), bromates, iodates, nitrates, dichromates (*e.g.*, $K_2Cr_2O_7$), and permanganates (*e.g.*, $KMnO_4$).

The production of oxygen by heating nitre, when potassium nitrite is left as a residue, has already been described (p. 43): $2KNO_3 = 2KNO_2 + O_2$. The method is not used in the preparation of oxygen, as a high temperature is required.

Potassium chlorate, $KClO_3$, is the most convenient source of oxygen in the laboratory. The crystals, which are anhydrous, melt at 372°, and on heating to 380° in a hard glass flask bubbles of oxygen are evolved: (1) $2KClO_3 = 2KCl + 3O_2$. As the reaction proceeds, the evolution of oxygen slackens, and the salt becomes pasty, finally almost solid, although decomposition is not nearly complete, *i.e.*, the residue is not wholly potassium chloride, KCl.

At this stage of the reaction the residue contains potassium chloride and **potassium perchlorate,** $KClO_4$, a salt richer in oxygen than the chlorate, which is produced by the reaction : (2) $4KClO_3 = 3KClO_4 + KCl$. The KCl and $KClO_4$ may be separated by treatment of the cooled residue with cold water, when the former salt dissolves. (*Cf.* p. 372.) If the temperature is raised when the salt becomes pasty, the mass fuses again, oxygen is evolved, and finally, when all has become solid, potassium chloride is left : (3) $KClO_4 = KCl + 2O_2$. Reactions (1) and (2) proceed simultaneously and independently from the commencement.

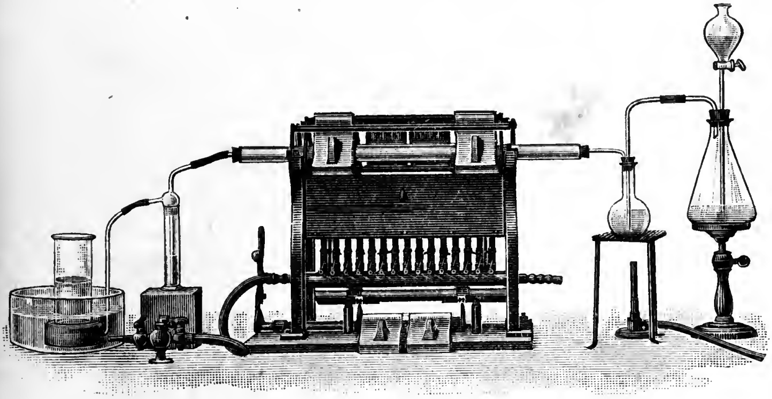


FIG. 80.—Decomposition of Steam by Chlorine.

At high temperatures another mode of decomposition : (4) $4KClO_3 = 2K_2O + 2Cl_2 + 5O_2$, takes place to a slight extent, the gas containing a little chlorine, and showing a slight fog, due to suspended solid potassium oxide, K_2O. A mixture of potassium and sodium chlorates liberates oxygen at a lower temperature than potassium chlorate alone.

Potassium permanganate on heating to 240° in a glass tube evolves very pure oxygen, leaving a black powdery residue of potassium manganate, K_2MnO_4, and manganese dioxide : $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$. By adding a *little* water to the residue, a dark green solution of the manganate is formed.

Many other oxy-compounds may be used as sources of oxygen gas. Thus, if a solution, or paste, of **bleaching powder** or **chloride of lime,** containing the compound CaO_2Cl_2, is heated to 75° with a few drops of cobalt or nickel chloride solution, oxygen is rapidly evolved (Mitscherlich, 1843):

$$CaO_2Cl_2 = CaCl_2 + O_2.$$

If a little manganous sulphate is added, the oxygen is free from chlorine. A solution of bleaching powder alone decomposes only slowly. Cobalt or nickel oxides are precipitated by the free lime contained in the bleaching powder: $CoCl_2 + Ca(OH)_2 = CoO + CaCl_2 + H_2O$. A higher, unstable oxide, Co_2O_3 or CoO_2, appears to be alternately formed and reduced, thus acting as a **carrier of oxygen**: $2CoO + CaO_2Cl_2 = 2CoO_2 + CaCl_2 = 2CoO + O_2 + CaCl_2$ (Fleitmann, 1865). A mixture of copper and ferrous sulphates, neither of which alone is active, accelerates the decomposition of bleaching powder solution (Jaubert). The same reaction occurs if chlorine gas is passed into boiling caustic soda solution, or milk of lime, to which a few drops of cobalt or nickel chloride have been added: $4NaOH + 2Cl_2 = 4NaCl + 2H_2O + O_2$.

EXPT. 62.—Add a little nickel chloride solution to a solution of caustic soda: a light green precipitate of the hydrated lower oxide, NiO,H_2O, is thrown down. Pour a little of the suspension of this into bleaching powder solution. The precipitate at once becomes oxidised to a black substance, Ni_2O_3,xH_2O, and oxygen is freely evolved on warming.

Chromium trioxide and **potassium dichromate** evolve oxygen when heated in a flask with concentrated sulphuric acid, the red colour of these compounds changing to the dark green colour of chromium sulphate, $Cr_2(SO_4)_3$:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + 2CrO_3 + H_2O$$
$$2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O.$$

Chromium trioxide also decomposes when heated alone, although a little sublimes unchanged: $4CrO_3 = 2Cr_2O_3$ (green) $+ 3O_2$.

If the residue left after decomposing potassium dichromate with sulphuric acid is cooled, diluted with an equal volume of water, and allowed to stand for some time in a loosely-covered beaker, beautiful deep-violet octahedral crystals of **chrome alum,** $K_2SO_4,Cr_2(SO_4)_3,24H_2O$, separate out.

Potassium permanganate explodes violently when warmed with concentrated sulphuric acid, but readily yields very pure oxygen if ordinary **hydrogen peroxide** (4 per cent. solution) is mixed with a solution of the permanganate acidified with dilute sulphuric acid: the two highly oxidised compounds mutually decompose each other, yielding a nearly colourless solution:

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Expt. 63.—A solution of 5 gm. of $KMnO_4$ in a cooled mixture of 100 c.c. of water and 50 c.c. of concentrated sulphuric acid is dropped from a tap-funnel into 100 c.c. of "10 volumes" hydrogen peroxide in a flask (Fig. 81). The evolved oxygen is collected over water.

The preparation of oxygen in the laboratory.—The evolution of oxygen from potassium chlorate is greatly accelerated if manganese dioxide is mixed with the salt.

Expt. 64.—Fuse a little potassium chlorate in a test-tube, and keep the temperature below the point at which oxygen is evolved. Now add a little powdered manganese dioxide: a rapid evolution of oxygen occurs.

If enough manganese dioxide is ground in a mortar with potassium chlorate to render the mixture black, and this **oxygen mixture** is heated in a glass tube or flask, decomposition occurs rapidly at a temperature below the melting point of the chlorate, oxygen being freely evolved. The heating must be carefully regulated, as the decomposition of potassium chlorate, unlike that of mercuric oxide (p. 24), *evolves* heat, and under certain conditions may become explosive.

The manganese dioxide undergoes no permanent chemical change in the reaction: it may be completely recovered by washing out the potassium chloride from the residue with water. The oxygen prepared in this way contains a little chlorine, which may be removed by washing with caustic soda solution; the gas is often misty from suspended particles of potassium chloride or hydroxide, the latter formed from water and potassium oxide (equation (4) on p. 161). These subside on standing over water.

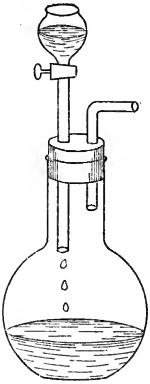


Fig. 81. Preparation of Oxygen from Potassium Permanganate and Hydrogen Peroxide.

Expt. 65.—Mix 25 gm. of powdered potassium chlorate with a few grams of powdered manganese dioxide in a mortar. Place the mixture in a wide test-tube, and tap the tube so as to leave a free passage for the gas from the bottom of the tube. Fit the tube, with a good cork and a wide (½-in.) glass delivery tube, to a Woulfe's bottle containing caustic soda solution, as shown in Fig. 82. The caustic soda removes any trace of chlorine from the gas. Support the test-tube in a horizontal position in a clamp, and heat the mixture gently with a slightly luminous flame, beginning at the end near the cork and moving towards the closed end as the reaction proceeds. If the evolution of gas becomes violent, withdraw the flame till it slackens. The gas may be collected in jars over water, or in a metal Pepys' **gas-holder,** as shown. The latter stands in a trough of water, and the delivery tube is inserted into the lower opening. When the gas has been collected, this opening is closed by a screw stopper. The funnel tube, *A*, and gas-holder are filled with water before the collection of the gas. When the gas is no longer evolved, the test-tube is taken off to prevent liquid being drawn back into the tube and cracking it. Jars may be filled in the upper trough of the gas-holder over the short tube, *B*, by opening the taps on *A* and *B*.

Warning.—Manganese dioxide has sometimes been adulterated with powdered coal; it then explodes violently on heating with chlorate. More than one death has been caused in this way, and a *little* of the mixture should always be heated in an open test-tube before beginning the experiment, in order to be sure that no deflagration occurs.

Other oxides, such as ferric oxide, cupric oxide, and chromium oxide, act similarly to manganese dioxide: they are also left unchanged after the reaction. This action of manganese dioxide, discovered by Döbereiner in 1832, is an example of numerous reactions in which a substance accelerates a chemical change without itself, apparently, taking part in the reaction. Such substances were called **catalysts** by Berzelius (1835).

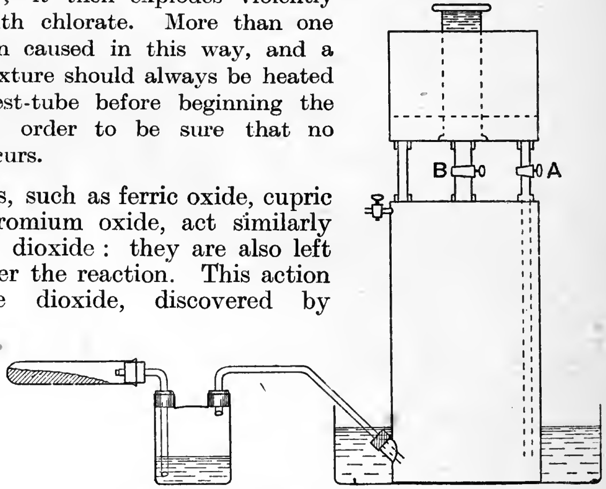


FIG. 82.—Preparation of Oxygen from Potassium Chlorate and Manganese Dioxide.

Combustion.—The combination of substances with oxygen, when attended with the evolution of heat and light, is called **combustion.** Substances which burn in air do so with greatly enhanced brilliancy in pure oxygen, since the nitrogen in air acts as a diluent, absorbing part of the heat given off in the combustion.

The combustion of **sulphur, phosphorus,** and **carbon,** giving acidic oxides, has already been described (p. 49):

$S + O_2 = SO_2$; $SO_2 + H_2O = H_2SO_3$ (sulphurous acid).
$2S + 3O_2 = 2SO_3$; $SO_3 + H_2O = H_2SO_4$ (sulphuric acid)
$4P + 5O_2 = 2P_2O_5$; $P_2O_5 + H_2O = 2HPO_3$ (metaphosphoric acid).
$C + O_2 = CO_2$; $CO_2 + H_2O = H_2CO_3$ (unstable carbonic acid).

The substances are conveniently burnt in globes of oxygen inverted over upright deflagrating spoons (Fig. 83).

Magnesium ribbon, if ignited in air and inserted into a jar of oxygen, burns with a blinding white light, forming white solid magnesium oxide, MgO, which is a weakly basic oxide, and turns red litmus paper blue when moistened and laid upon it. **Sodium** and **potassium,** when heated in iron deflagrating spoons until they begin to burn, and then lowered into *dry* jars of oxygen, burn with bright yellow and purple flames, respectively, forming orange-yellow solid oxides which dissolve in water with evolution of oxygen and formation of strongly alkaline sodium and potassium hydroxides :

$2Na + O_2 = Na_2O_2$ (sodium peroxide) ; $2Na_2O_2 + 2H_2O = 4NaOH$ (caustic soda) $+ O_2$;

$2K + 2O_2 = K_2O_4$ (potassium tetroxide) ; $2K_2O_4 + 2H_2O = 4KOH$ (caustic potash) $+ 3O_2$.

A spiral of **iron** wire, tipped with a bit of burning wood, burns brilliantly, giving off a shower of bright sparks, when lowered into a bottle of oxygen. Black oxide of iron, Fe_3O_4, is formed in fused globules, which crack the bottle when they fall on it, even if water is poured into the bottle before the experiment.

A jet of **hydrogen** burns in a jar of dry oxygen, producing water, which condenses in drops on the cold sides of the jar : $2H_2 + O_2 = 2H_2O$. If a jet of oxygen is thrust into an inverted jar of hydrogen, burning at the mouth, the oxygen takes fire, and continues to burn in the atmosphere of hydrogen (Fig. 84). The terms **combustible,** and **supporter of combustion,** are, therefore, purely relative.

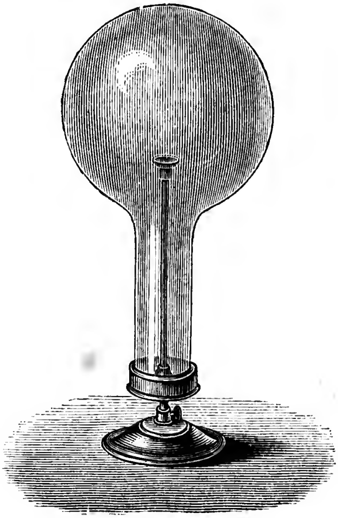


FIG. 83.—Apparatus for Combustions in Oxygen.

EXPT. 66.—Dry barium or strontium chlorate is heated in a vertical spoon until it evolves oxygen freely. A globe of coal gas is then lowered over the spoon into water in the trough (Fig. 83). The oxygen from the chlorate, if the latter is sufficiently heated, takes fire, and burns in the coal gas, the flame being coloured intensely green or crimson by the volatile barium or strontium compounds, respectively.

Many combustible substances, in a finely divided condition, ignite spontaneously in air or oxygen.

Expt. 67.—By means of a brush trace letters on a piece of filter-paper with a solution of phosphorus in carbon disulphide. When the solvent evaporates, the finely divided phosphorus ignites, leaving the charred letters on the paper.

Expt. 68.—Precipitate a solution of lead acetate with a solution of Rochelle salt, $KNaC_4H_4O_6$. The white precipitate of lead tartrate, $PbC_4H_4O_6$, is filtered, washed, and dried in a steam-oven. Small portions are placed in narrow tubes, sealed at one end and drawn out at the other. The tartrate is heated until fumes are no longer evolved, and the tubes are sealed. If a tube, after cooling, is cut with a file, and the finely divided lead shaken out, the metal glows brightly, forming yellow fumes of lead oxide, PbO. This form of the metal is called **pyrophoric lead.**

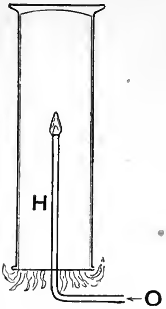


Fig. 84.
Oxygen burning in Hydrogen.

Many substances, such as phosphorus, oxidise slowly when exposed to air or oxygen, without catching fire, because the heat produced is dissipated too rapidly to raise the mass to the ignition point. Oily cotton-waste, however, may become heated to the ignition point if stored in heaps exposed to air. This slow process of oxidation is known as **autoxidation.**

Oxygen is **absorbed** from gaseous mixtures by: (i) a solution of pyrogallol in caustic potash, which turns black (160 grams of KOH, 10 grams of pyrogallol, 130 c.c. of water); (ii) moist phosphorus (this does not glow in pure oxygen); (iii) an acid solution of chromous chloride, $CrCl_2$, which turns from blue to green, owing to the formation of chromic chloride: $4CrCl_2 + O_2 + 4HCl = 4CrCl_3 + 2H_2O$; (iv) by mixing the gas with excess of hydrogen, and passing over platinum black at 100°, or platinised asbestos at a dull red heat, when water is formed; one-third of the contraction of the gas then represents the oxygen contained in it: $2H_2 + O_2 = 2H_2O$ (liquid).

Catalysis.—The action of manganese dioxide, copper oxide, and ferric oxide in promoting the decomposition of potassium chlorate by heat, and the similar effect of cobalt and nickel oxides on bleaching powder, have been described. These substances appear to act by contact, hence their effect was called **contact action** by Mitscherlich; the usual name, due to Berzelius, is **catalytic action** or **catalysis.** The manganese dioxide is called a **catalyst.**

A catalyst is a substance which alters the speed of a chemical reaction without itself undergoing permanent chemical change; in most cases it accelerates the reaction, when it is called simply a catalyst, but in some cases it retards it, when it is called a **negative catalyst.** It is essential that a true catalyst shall undergo no *permanent* chemical change; it must be left after the reaction of the same chemical composition as at the beginning, but not necessarily in the same physical state. Very small quantities of a catalyst will therefore serve to bring about the decomposition, or other chemical change, of large quantities of materials. The importance of catalysts in chemical industry is therefore clear.

The first reasonable **theory of catalytic action** was due to J. Mercer (1842). This assumed that the catalyst forms with one of the final products of reaction an unstable **intermediate compound,** which then breaks up, reproducing the catalyst in its original chemical composition, and liberating the product of reaction. This series of alternating, or **cyclic reactions,** so called because the catalyst goes through a series of complete cycles of changes and returns to its original state after each, is regarded by this theory as the cause of catalytic action. Thus, manganese dioxide in presence of a powerful oxidising agent, such as potassium chlorate, tends to pass into a higher stage of oxidation, say Mn_2O_7, which would give potassium permanganate with the potassium salt. At the high temperature, however, this higher oxide can hold its oxygen only transiently; it breaks up, giving gaseous oxygen, and forming manganese dioxide again:

$$KClO_3 + 2MnO_2 \rightarrow KCl + Mn_2O_7 \rightarrow KCl + 2MnO_2 + 3O.$$

Fowler and Grant (1890) showed that only oxides which can form unstable higher oxides, again decomposed by heat, can act catalytically in the decomposition of potassium chlorate. Thus, $MnO_2 \rightarrow MnO_3$ or Mn_2O_7; $Cr_2O_3 \rightarrow CrO_3$; $Fe_2O_3 \rightarrow FeO_3$; all these higher oxides are known in the form of salts: K_2O,MnO_3 (manganate); K_2O,Mn_2O_7 (permanganate); K_2O,CrO_3 (chromate); K_2O,FeO_3 (ferrate). Copper oxide probably forms an imperfectly known higher oxide (? CuO_2). Oxides which do not form higher oxides, such as zinc oxide or magnesium oxide, act only very feebly (to the same extent as powdered glass), whilst acidic oxides, such as alumina, Al_2O_3, vanadium pentoxide, V_2O_5, or tungsten trioxide, WO_3, give both chlorine and oxygen: $2KClO_3$ (or K_2O,Cl_2O_5) + $WO_3 \rightarrow K_2O,WO_3 + Cl_2O_5 \rightarrow K_2O,WO_3 + Cl_2 + 5O$.

EXPT. 69.—Fuse some potassium chlorate in two hard glass tubes. To one add a *very small* quantity of manganese dioxide, to the other a very small quantity of chromium sesquioxide, Cr_2O_3. Observe that (i) oxygen is evolved; (ii) the fused salt becomes permanently pink ($KMnO_4$), and yellow (K_2CrO_4), respectively. $KMnO_4$ cannot exist alone at the temperature of the fused chlorate, hence it must be continuously decomposed and reproduced by a series of cyclic actions such as that described above. A little ferric oxide, Fe_2O_3, produces a violent effervescence, and on cooling the mass is slightly pink, from the formation of ferrate, K_2FeO_4.

McLeod (1889) observed that pieces of manganese dioxide put into fused chlorate break up into a very fine powder. The *physical* state of the manganese dioxide changes, which suggests that it has entered into reaction and been reproduced. Traces of chlorine are always evolved in the preparation of oxygen from chlorate, and McLeod suggested that chlorine and potassium permanganate are intermediate products in the decomposition:

(1) $2KClO_3 + 2MnO_2 = 2KMnO_4 + Cl_2 + O_2$.
(2) $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$.
(3) $K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2$.

If chlorine escapes, however, the residue should contain manganate; this is never found, so that probably the chlorine is produced by a secondary reaction: $4KClO_3 = 2K_2O + 2Cl_2 + 5O_2$, which is known to take place at 360°. Reactions (2) and (3) are also known to take place, but it is doubtful if (1) occurs. This reaction, however, is the basis of McLeod's scheme. No perchlorate is formed.

It may be difficult to see how manganese dioxide can exert any action on *solid* chlorate, since the catalytic effect occurs below the fusion point of the latter. But some local fusion probably occurs on account of the heat evolved in the reaction (flashes of light are always seen), and in any case L. H. Parker (1914–18) has shown that chemical action may occur between solids. Thus, he found that the reaction:

$$BaCO_3 + Na_2SO_4 = BaSO_4 + Na_2CO_3,$$

and the reverse reaction, take place to a limited extent when the dry powdered mixture is heated short of fusion, or simply triturated in a dry mortar. Reaction also occurs in the dry powder when it is strongly compressed, as was shown by Spring.

Manufacture of oxygen.—On the large scale oxygen is prepared (1) from **water**, by electrolysis (p. 56); (2) from **air**. In the preparation from air two kinds of processes are used: (*a*) **physical methods**, (*b*) **chemical methods.**

All the **chemical methods** depend on the use of a substance, A, which takes up oxygen from the air under certain conditions, leaving the nitrogen: (i) $A + O_2 + 4N_2 = AO_2 + 4N_2$. Under other conditions the compound AO_2 can be broken up again into A, which is used over again, and oxygen: (ii) $AO_2 = A + O_2$. Reactions (i) and (ii) alternate.

Boussingault in 1852 noticed that if **baryta,** BaO (which is a substance similar to quicklime, CaO), is heated in a porcelain tube to *dull redness*, it can absorb oxygen from air passed over, giving **barium peroxide**: (i) $2BaO + O_2 = 2BaO_2$, whilst the nitrogen is not absorbed. If the barium peroxide is now heated to *bright redness*, it gives off oxygen, leaving baryta: (ii) $2BaO_2 = 2BaO + O_2$. The reaction is therefore **reversible**, and proceeds in one direction or the other according to the temperature: $2BaO_2 \rightleftharpoons 2BaO + O_2$. It was found that the baryta rapidly became inactive; carbon dioxide in the air produced barium carbonate, $BaCO_3$, which is only decomposed at a white heat, and the silica from the tube formed barium silicate, $BaSiO_3$. Both these substances cover the baryta. By using purified air, and iron retorts, the brothers Brin in 1879 succeeded in keeping the baryta active. They found that the process could be worked at one temperature if, during the absorption, the air was under 2 atm. pressure, whilst the peroxide was decomposed on reducing the pressure to about 2 in. of mercury. The iron retorts were placed vertically in a furnace heated by gas to about 700°. This **Brin process** was the principal technical method until 1902; it has now given way to the liquid air process (p. 175).

Tessié du Motay in 1866 passed air over a mixture of caustic soda and manganese dioxide heated to dull redness in retorts. **Sodium manganate** was produced:

$$\text{(i)}\ 2MnO_2 + 4NaOH + O_2\,(\text{air}) = 2Na_2MnO_4 + 2H_2O.$$

The temperature was then raised to a bright red heat, and steam passed over the manganate, when oxygen was liberated:

$$\text{(ii)}\ 2Na_2MnO_4 + 2H_2O = 2MnO_2 + 4NaOH + O_2.$$

The temperature was allowed to fall, and air passed over the residue; manganate was again formed. Reactions (i) and (ii) thus alternated. The process was at one time used in Paris, but has been entirely abandoned.

Kassner in 1889 heated a mixture of litharge and chalk in air at 600°. This gave **calcium plumbate**, $2CaO, PbO_2$, or Ca_2PbO_4:

$$\text{(i)}\ 4CaCO_3 + 2PbO + O_2\,(\text{air}) = 2Ca_2PbO_4 + 4CO_2.$$

Moist furnace gas was passed over the plumbate at 80–100°:

$$\text{(ii)}\ Ca_2PbO_4 + 2CO_2 = 2CaCO_3 + PbO_2.$$

On heating to 500°, the PbO_2 was decomposed, with evolution of oxygen, leaving PbO and $CaCO_3$. This process is complicated, and is not used.

A few **physical processes** were proposed before the present industrial method was adopted. Graham found that oxygen passes through an unvulcanised rubber membrane two and a half times as fast as nitrogen, and by pumping air through a rubber bag by means of a mercury pump he obtained a gas containing 42 per cent. of oxygen, which rekindled a glowing chip. This process, depending on the selective permeability of a membrane, is called **dialysis.** Again, if air is shaken with water, oxygen is **dissolved** more readily than. nitrogen, and the gas liberated on heating or reducing the pressure is richer in oxygen (p. 97). By working under pressure, and repeating the process four or five times, Mallet obtained a gas containing over 75 per cent. of oxygen.

If air is slowly passed through the stem of a clay tobacco-pipe enclosed in a partially exhausted glass tube, the lighter nitrogen **diffuses** through the porous tube more rapidly than the oxygen, in the inverse ratio of the square roots of the densities (Graham):

$$\frac{\text{Speed of diffusion of nitrogen}}{\text{Speed of diffusion of oxygen}} = \frac{\sqrt{16}}{\sqrt{14}} = \frac{1{\cdot}07}{1{\cdot}00}$$

The issuing gas is therefore richer in oxygen than air. This process was called **atmolysis** by Graham.

Since oxygen is slightly heavier than nitrogen, Mazza (1901) attempted to separate air into the two gases by passing it through a centrifugal sieve: needless to say, the method failed.

The only process now used for the manufacture of oxygen is the **fractional distillation of liquid air.**

Liquefaction of gases.—Sulphur dioxide was liquefied by cooling and pressure by Monge and Clouet; in 1805 chlorine and ammonia were reduced to the liquid state by Northmore. In 1823 liquid chlorine was again obtained by Faraday, by warming chlorine hydrate in one limb of a sealed Λ-tube, the other limb of which was cooled in a freezing mixture. In later experiments, Faraday was able to liquefy hydrogen sulphide, hydrogen chloride, carbon dioxide, nitrous oxide, cyanogen, and ammonia; but oxygen, nitrogen, and hydrogen resisted all attempts to reduce them to the liquid state.

Most of the attempts relied on the application of pressure to the gases. Some gases may be liquefied by the application of pressure without very strong cooling: in the following table the pressures in atm. required to liquefy the gases at 0° are given:—

Sulphur dioxide	1·54	Ammonia	4·19
Chlorine ...	3·66	Carbon dioxide	39·0 (at 15°)

The application of pressures up to 2000 atm., however, was tried by Natterer in the case of the gases nitrogen, oxygen, and hydrogen, without result.

In 1869 Andrews discovered that a gas cannot be liquefied by any pressure, however high, unless it is previously cooled below what is called the **critical temperature** of the gas. Just below this temperature the gas is liquefied by the application of what is known as the **critical pressure.** The volume occupied by 1 gm. of a substance at the critical temperature and under the critical pressure is called the **critical volume.**

The critical temperatures of the so-called **permanent gases** lie below the lowest temperatures attained by the older experimenters. As soon as it was clear that strong cooling was necessary in the case of these gases, and that high pressures alone could never succeed, the problem was solved, independently, by Pictet and Cailletet in 1879.

Pictet used the apparatus shown in Fig. 85. Oxygen was generated in the retort *P* by heating potassium chlorate, and was compressed by its formation in the copper tube *O*, fitted with a pressure gauge *Q* and release valve *N*, cooled in liquid carbon dioxide *L* boiling under reduced pressure. This carbon dioxide was again liquefied by the pump *G* in a second copper tube, *EF* surrounded by liquid sulphur dioxide boiling under reduced pressure, and circulated by a second pump *A*. Pictet got the temperature down to − 140°, and the pressure rose to several hundred atmospheres. On opening the release-valve, a jet of liquid oxygen issued from it, at once boiling away.

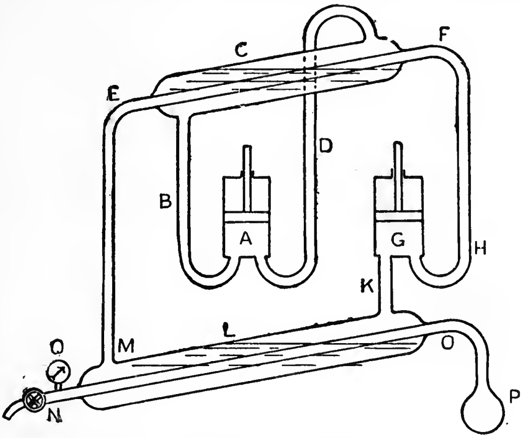


FIG. 85.—Liquefaction of Oxygen by Pictet.

Cailletet compressed the gas by a powerful pump forcing water into a strong steel vessel, *B*, Fig. 86, in which the gas was contained in a tube, *T*, sealed below by mercury. As water was forced into *B*, the mercury was driven into the gas tube, and the gas strongly compressed. The pressure was then suddenly released by opening a valve which allowed the water to escape, and the gas expanded suddenly. The expansion was so rapid (**adiabatic expansion**) that the cooling produced, by the gas doing work against pressure in expanding, reached the point of liquefaction of the oxygen. A fog of liquid droplets was seen momentarily in the tube, at once vanishing as heat was communicated from the walls of the latter.

Liquid air.—The liquefaction of air in bulk was effected in 1895, independently, by Hampson in England and by Linde in Germany. These inventors made use of a new principle, viz., the **Joule-Kelvin effect,** investigated by Joule and William Thomson (later Lord Kelvin) in 1852–62. A compressed gas was allowed to escape, through a plug of silk in a boxwood tube, into the free air, and a slight cooling effect was then noticed with most gases (air, oxygen, nitrogen, carbon dioxide), or, with hydrogen alone, a slight heating effect.

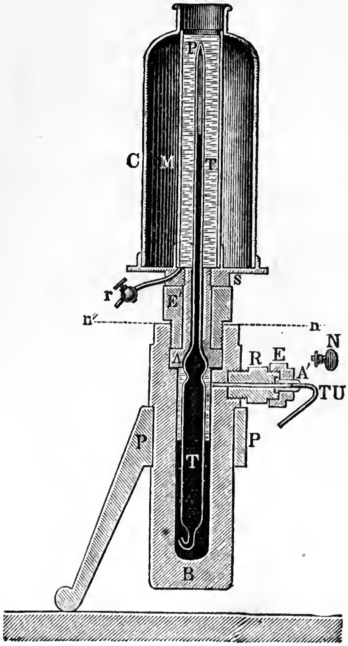


FIG. 86.—Liquefaction of Gases by Cailletet.

This temperature change is quite different from that due to the *external* work done by a gas in adiabatic expansion. If a given mass of gas, of volume v (Fig. 87), is forced under a pressure p_1 through the plug into a space under a lower pressure p_2 (say $\frac{1}{2}$ p_1), it occupies a larger volume v_2 (say 2 v_1). The work done *on* the gas is p_1v_1, that done *by* the gas is p_2v_2. If the gas obeyed Boyle's law, $p_1v_1 = p_2v_2$ ($v_2 = 2v_1$; $p_1 = 2p_2$), so that no *external* work would be done on the whole, and if no other effect were involved, there would be no change of temperature. Since, however, v_2 is greater than v_1, the molecules of the gas will have been separated, and if an attraction exists between them, work will have been spent on the gas in separating the molecules. With hydrogen, a slight *repulsion* appears to exist between the molecules. The energy required for this *internal* work is taken from the heat of the gas, and a slight cooling effect therefore results. Usually, both external and internal work are involved. Thus, in the case of air, p_2v_2 is slightly larger than p_1v_1, since the gas is slightly more compressible than an ideal gas; and p_1 is greater than p_2. A little heat is absorbed in providing this extra work, $p_2v_2 - p_1v_1$, but more is needed for the internal

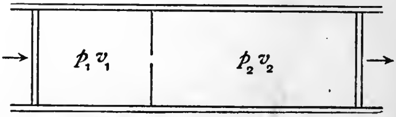


FIG. 87.—Diagram illustrating Free Expansion of Gases.

work due to the expansion against the slight attractive forces exerted between the molecules.

In the case of air the cooling effect is given by the formula:

$$\textbf{Cooling effect in degrees C.} = \frac{\text{difference of pressures in atm.}}{4} \times \left(\frac{273}{T_1}\right)^2,$$

where T_1 is the absolute temperature of the air before expansion.

Thus, if air at 0°, and under a pressure of 100 atm., is expanded through a valve to atmospheric pressure, the fall of temperature will be $\frac{99}{4} \times \left(\frac{273}{273}\right)^2 = 24{\cdot}7°$. Now suppose this cool air, at $-24{\cdot}7°$, is allowed to sweep over the surface of a copper pipe bringing the compressed air to the valve, by placing the latter inside the pipe taking away the cold expanded air (Fig. 88). The expanded air will abstract heat from the air coming to the valve, becoming itself warmed nearly to the atmospheric temperature. The cooled compressed air after expansion also becomes 24·7° colder, and this still colder air at $-49{\cdot}4°$ sweeps over the inner tube, reducing still further the temperature of the compressed air coming down. The cooling effect thus *accumulates,* and after an interval the air issuing from the nozzle becomes so cold that it liquefies. This apparatus, called a **heat-interchanger,** was applied by Hampson and by Linde to the liquefaction of air on a large scale. The two forms of apparatus are very similar in principle. Fig. 89 shows the apparatus used at University College, London.

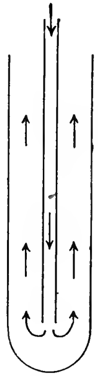


FIG. 88. Cooling of Gases by Free Expansion.

Air is drawn through a purifier and filter, *A*, to the compressor, *BD*, in which the double-acting pistons are lubricated with water. The air is first compressed in *B*, passes through the intercooler, *C*, immersed in water, to the cylinder, *D*, where it is brought to 200 atm. The moist air, heated by compression, passes through the cooling coil, *E*, to the strong steel vessel, *F*, where liquid water is deposited. Water vapour and carbon dioxide (which would solidify and choke up the liquefier) are removed by solid caustic soda in the vessel *H*, and the dry, cool, strongly compressed air then passes down a long spiral of small-bore copper tubing in the interchanger, *K*, to the expansion valve, *L*, which can be adjusted from outside at *M*. The air, strongly cooled by expansion, sweeps up over the outer surface of the coils in *K*, thereby cooling the compressed air coming down. Liquid air finally escapes from *L*, and collects in the vacuum-walled Dewar vessel, *N* (see below), from the inner vessel of which it is drawn off through the valve, *O*. The heat-interchanger is surrounded by a carefully lagged casing to prevent inflow of heat from outside. The liquid is received in double-walled **Dewar flasks** (Fig. 90), the inner surfaces of which, silvered to reflect heat, have a high vacuum between them to cut down heat transmission to a minimum.

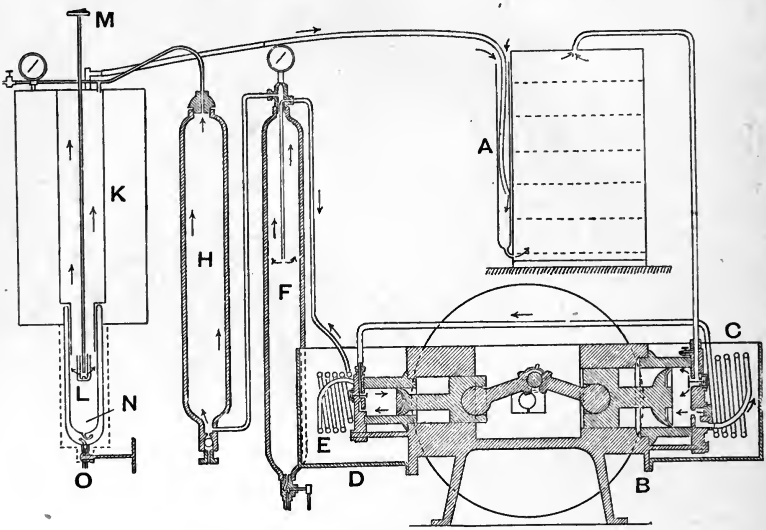


FIG. 89.—Apparatus for Liquefaction of Air.

Liquid air, as it issues from the valve, is usually slightly turbid, because it contains particles of solid water and carbon dioxide from the surrounding air. If filtered through a large filter paper it forms a clear liquid, with a pale blue colour. If poured out into the air, it evaporates, producing thick white clouds of condensed moisture. Its temperature is about − 190°, and when exposed to this extreme cold many substances undergo remarkable changes in properties. Lead becomes brittle, and rubber extremely hard and brittle. Mercury is at once frozen to a malleable solid. Raw meat, fruits, flowers, etc., become hard, and can be reduced to powder in a mortar. A kettle containing liquid air "boils" briskly when placed on a slab of ice, and copious clouds of

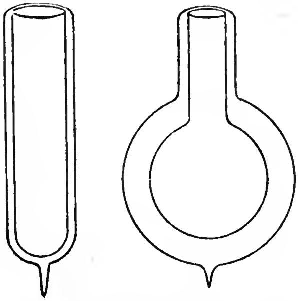


FIG. 90.—Dewar Vacuum Vessels.

"steam," *i.e.*, atmospheric moisture condensed to particles of ice by the cold of the escaping evaporated air, are emitted from the spout.

On standing, liquid air becomes bluer in colour; the more volatile colourless liquid nitrogen (b. pt. — 194°) escapes, and sky-blue **liquid oxygen** (b. pt. — 182·5°) is left.

The fractionation of liquid air.—In order to obtain **liquid oxygen** from liquid air, it would appear simplest to allow the liquid to evaporate slowly in a Dewar flask, when the nitrogen would pass off and oxygen be left. This would, however, lead to serious loss of oxygen, as is seen from the table below:

Percentage of liquid not evaporated.	Percentage of oxygen in liquid by weight.	Percentage of oxygen in gas evaporating.	Percentage of original oxygen left in liquid.
100	23·1	7·5	100
50	37·5	15	80
30	50·0	23	65
20	60·0	34	52
15	67·5	42	43
10	77·0	52	33
5	88·0	70	19

The gas coming from fresh liquid air contains only 7·5 per cent. of oxygen; when the evaporation has proceeded until the liquid contains 50 per cent. of oxygen, or about two-thirds of the liquid has evaporated, the gas is of the same composition as ordinary air. It is only when 95 per cent. of the liquid has disappeared that the gas contains 90 per cent. of oxygen, and if the remaining liquid is evaporated to produce this rich gas, we can recover only 19 per cent. of the oxygen originally present in the liquid air.

Linde (1902) avoided this loss by making use of a **rectifying column**, in which the escaping gas is scrubbed by liquid passing down in the opposite direction.

The air is compressed to 180 atm., cooled to — 15° in an ammonia refrigerator, and passed to the rectifying column, *K* (Fig. 91), by the tube *a*, which divides into three copper tubes, *b*, enclosed in a wider tube, *c*, passing outside the column to form a heat-interchanger. At the bottom the three tubes again unite in a single tube, *d*, which passes as a spiral coil inside an iron vessel, *F*, continuing as the tube *f* to the valve *g*, where the pressure falls to about 1¼ atm. The cold expanded air passes to the small reservoir, *H*, at the top of the rectifying column, *K*, whence it leaves by the tube *l*. At *l′* it enters the large tube *c*, passing through this in the opposite direction to the compressed air coming down the triple coil, and taking heat from the latter. The expanded air finally leaves at *c′*, at — 15°, to the pre-cooler, escaping from this, warmed to — 5° to — 6°, to the free air. The cooling thus accumulates until liquid appears, which collects in *H*, and finally overflows down the column *K*, collecting in *F*. This is evaporated by the heat given out from the air inside the coil *e*, and the vapour, which is mainly nitrogen, passes up the rectifying column. Here it is scrubbed by the descending liquid, the latter abstracting nearly all the oxygen from the gas, which leaves by the tube *l*. The accumulating liquid oxygen now rises in the tube *m*, and gradually evaporates, the cold gas passing up one of the tubes of the triple spiral, where it takes up heat from the incoming gas, until it is warmed nearly to the atmospheric temperature. The gas leaves at *m′* to the gas-holders, from which it is taken by pumps and compressed into steel cylinders to 120 atm. When the apparatus has got into steady operation, the working pressure is reduced from 180 to 90 atm. The gas so produced contains 95 per cent. of oxygen and 5 per cent. of nitrogen.

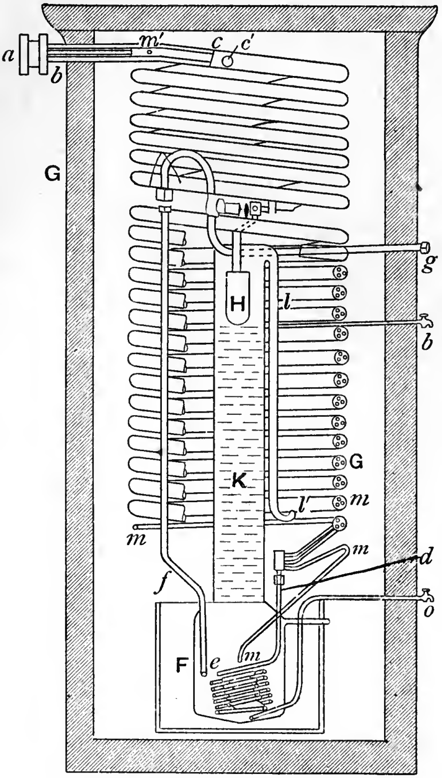


Fig. 91.—Linde's Oxygen Apparatus.

Claude in 1906 introduced two new principles: (1) he liquefied the air in stages, obtaining finally two liquids, one rich in oxygen and the other in nitrogen; (2) the expanding gas was allowed to do work in an engine cylinder containing a piston, and the heat equivalent of this external work was taken from it. (This had been previously suggested by Rayleigh.) The piston is first lubricated with petroleum ether, and then with liquid air itself. A taller rectifying column is used, the liquid rich in nitrogen being discharged into the top, whilst the liquid rich in oxygen is introduced at a point lower down, where the descending liquid has become enriched to the same composition.

Claude's apparatus is shown in Fig. 92. Compressed air, cooled by an interchanger as in the Linde process, enters *A*, into a vessel containing two series of vertical pipes. The first drain into *A*, and the second form a ring round the first and drain into *C*. Both sets are immersed in the bath, *S*, which, when the machine is operating, contains nearly pure liquid oxygen.

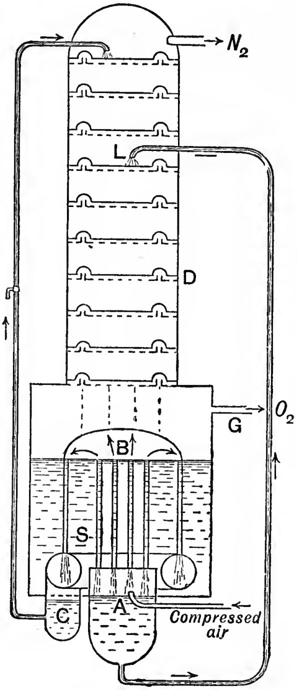


Fig. 92.—Claude's Oxygen Apparatus.

The condensation of the compressed air evaporates a portion of this oxygen, part of the vapour going up the rectifying column, *D*, where it is practically completely condensed, displacing nitrogen from the liquid, and returns to *S*. The rest of the vapour goes off by the pipe *G* to the heat-interchanger. So far, the process is identical with that of Linde. The difference lies in the way in which the compressed air is condensed. It passes up the central group of pipes in *S*, and a liquid condenses there which is relatively rich in **oxygen,** which drains back into *A*. The gaseous residue passes through the outer ring of pipes, liquefies in them, and falls into *C*, the liquid consisting almost wholly of **nitrogen.** The liquid in *C* is then taken to the top of the column, that in *A* to a lower compartment *L*, containing scrubbed liquid of the same composition. Almost pure nitrogen gas escapes at the top of the column. The liquid condensed in the inner pipes is scrubbed by air passing on.

In England there are now twelve plants, producing an aggregate of one million cu. ft. of oxygen gas, or 118 tons, per day, as compared with less than one-sixth of that production in 1911. This appears large, but in Germany a single unit plant is capable of producing nearly as much as the whole dozen English works.

Liquid air is stored in spherical **metallic vacuum vessels,** holding 5–30 galls., the inner vessel being suspended by a thin metallic neck, and the annular space highly exhausted (Fig. 93). The high vacuum is maintained by means of a tube of absorbent charcoal, open at the end exposed to the vacuous space, and with the other (closed) end immersed in the liquid air itself. The daily rate of loss does not exceed 5 per cent.

When used in connection with **aviation,** a smaller metallic vacuum vessel is provided with a mechanism for controlling the rate of evaporation of the liquid oxygen, and a tube leading to the inhaling mouth-piece. The controlling mechanism consists of a siphon dropping liquid oxygen at a controlled rate into an evaporating chamber. This control is necessary, since great fluctuations in the rate of evaporation are caused by movements from higher to lower altitudes where the atmospheric pressure is higher.

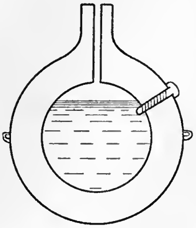


Fig. 93.
Metallic Vacuum Vessel.

About 85 per cent. of the oxygen made is used, in about equal proportions, for cutting and welding metals by the oxy-acetylene blowpipe (p. 189). The rest is used in medicine for treating cases of pneumonia, gas-poisoning, etc., for oxidising linseed oil, for maturing spirits, and in aviation.

The physical properties of oxygen.

Normal density 1·42906 gm. per litre.
Boiling point — 182·9°.
Freezing point — 219° /12 mm.
Density of liquid 1·1181 at b. pt.
Density of solid 1·4256 at — 222·5°.
Critical temperature — 118°
Critical pressure 50 atm.
Specific heat of gas at 20° to 400° 0·2419.
Specific heat of liquid 0·347.
Latent heat of evaporation : 50·97 at — 182·5° ; 55·5 at — 205°

Solubility in sea-water, 78 per cent. that in pure water (p. 97).

Liquid oxygen is strongly magnetic ; the gas is weakly magnetic.

EXERCISES ON CHAPTER X

1. How may oxygen be prepared by chemical methods from air and from water ? In what forms does the element occur in nature ?
2. What happens when the following substances are heated : mercuric oxide, potassium chlorate, potassium permanganate, manganese dioxide ? The following substances are heated with concentrated sulphuric acid : potassium dichromate, manganese dioxide, barium peroxide. What reactions occur ? Give equations.
3. Describe the preparation of oxygen from bleaching powder, and from potassium chlorate and manganese dioxide. How have the reactions been explained ?
4. What classes of oxides are known ? How was the formation of salts from acids and bases previously explained ?

5. What chemical methods for the manufacture of oxygen have been proposed ? Describe the Brin process.

6. Describe briefly the principle of the method used in the liquefaction of air. How is oxygen prepared from liquid air ?

7. Describe experiments which illustrate the combustion of substances in oxygen. Are the terms " combustible " and " supporter of combustion " entirely satisfactory ?

8. It is sometimes stated that " oxygen is obtained by the evaporation of liquid air." Discuss this statement. What is the process actually employed ?

9. What volumes of oxygen, measured over water at 15° and 750 mm. pressure, would be obtained by the decomposition of : (*a*) 25 gm. of potassium bromate by heat, (*b*) 250 c.c. of 5 per cent. hydrogen peroxide solution by acidified potassium permanganate ?

10. One hundred c.c. of air are shaken with 1 litre of water at 2 atm. pressure. The dissolved gas is then expelled by boiling, and the process repeated with 500 c.c. of water. What are the volume and composition of the gas finally obtained ?

CHAPTER XI

HYDROGEN. (H = 1)

Occurrence of hydrogen.—Although hydrogen appears to have been discovered by Paracelsus in the sixteenth century, and an inflammable gas (*gas pingue*) was described by Van Helmont (p. 31), it was first investigated by Cavendish in 1766.

In the **free state,** as the gas H_2, hydrogen occurs in traces in volcanic gases; those evolved in the eruption of Mt. Pelée in 1912 contained 22·3 per cent. H_2. It also occurs in small cavities in rock-salt, and in various minerals and rocks, such as apatite, serpentine, gneiss, blue-clay, Peterhead granite, basalt, and beryl. It occurs in the atmosphere, but only to the extent of about 1 part per million, and is thus found in the earlier fractions of the gases from liquid air. The **natural gas** from American oil-wells sometimes contains up to 20 per cent. by volume of hydrogen. Meteorites, composed chiefly of iron with nickel and cobalt, contain hydrogen brought from the stellar space to the earth. Spectroscopic investigation shows that the outer atmosphere of the sun consists largely of hydrogen; this gas is the chief constituent of the solar prominences, which are parts of the chromosphere and are seen during total eclipse as huge red flames of incandescent gas reaching out from the sun's disc sometimes as far as 300,000 miles into space. Hydrogen is produced by the decay of vegetable matter (cellulose), owing to the activity of certain bacteria, and is present in the gas from stagnant ponds (p. 672).

Hydrogen occurs, however, chiefly in **combination** with other elements, especially with oxygen, in the form of **water,** H_2O, which covers such a large part of the surface of the earth. Hydrogen is found in combination with carbon as **hydrocarbons;** the gas issuing from fissures in coal often consists of nearly pure **methane,** CH_4; more complicated hydrocarbons make up the **petroleum,** or mineral oil, of Russia, Persia, and North America. All **organic substances** in the animal and vegetable worlds, and coal, contain hydrogen, and other hydrogen compounds found in nature are sulphuretted hydrogen (H_2S), phosphoretted hydrogen (PH_3), ammonia (NH_3), and, in volcanic gases, the halogen compounds hydrochloric (HCl), hydrobromic (HBr), and hydriodic (HI) acids. All **acids** and **alkalies** contain hydrogen.

Hydrogen is prepared artificially from three main sources: (1) from **water,** H_2O, by removal of oxygen; (2) from **acids,** such as sulphuric acid, H_2SO_4, and hydrochloric acid, HCl, by the action of certain metals; (3) from **alkalies,** containing the hydroxyl group, OH, such as caustic soda, $NaOH$, and baryta, $Ba(OH)_2$, by the action of certain metals, or by electrolysis.

Hydrogen from water.—The name hydrogen was given to the element by Lavoisier, from the Greek *hudor*, water. Water may be decomposed with the liberation of hydrogen in a variety of ways.

By **electrolysis,** already described on p. 56, both hydrogen and oxygen are produced. The volumes of hydrogen and oxygen collected should, theoretically, be in the ratio of 2 to 1. In practice rather less oxygen is evolved, partly on account of the greater solubility of oxygen in water compared with hydrogen (1·8 to 1), and partly owing to oxidation of the sulphuric acid added to the water "to make it conduct the current."

The deficiency of oxygen is mainly due to the formation of **persulphuric acid,** $H_2S_2O_8$, at the anode. Some **hydrogen peroxide,** H_2O_2, is also formed. The presence of these oxidising agents in the liquid round the anode may be shown by adding a solution of potassium iodide and starch, when a blue colour, due to liberation of iodine, appears (p. 320). The oxygen evolved also contains a little **ozone,** O_3, and turns blue a piece of paper dipped in potassium iodide and starch solution. If the liquid is electrolysed hot, or phosphoric acid used instead of sulphuric acid, no ozone is formed and the volumes are very nearly in the ratio 2 : 1.

Hydrogen is also formed by the action of certain **metals** on water. **Sodium** and **potassium** react violently with cold water, the latter metal taking fire: $2Na + H_2O = 2NaOH + H_2$.

EXPT. 70.—Press a piece of clean sodium, not larger than a *small* pea, into a short length of narrow ($\frac{1}{4}$ in.) lead tubing, closed at one end, and hold this with tongs in a trough under an inverted jar of water. Hydrogen collects in the jar, and the water turns red litmus blue from the presence of caustic soda. (Explosions sometimes occur in this experiment.) A *small* piece of potassium thrown on water floats, and the hydrogen takes fire and burns with a purple flame, due to potassium vapour. A small fused globule of caustic potash (KOH) is left in the spheroidal condition; this is often projected from the water on cooling. The water contains caustic potash and turns red litmus blue. Sodium reacts in a similar way, but the hydrogen does not take fire unless the metal is kept in one place by throwing it on starch-jelly: the hydrogen then burns with a yellow flame, owing to the presence of sodium vapour.

The action of **sodium amalgam** on water is much less vigorous than that of sodium itself. The amalgam is made by dissolving sodium in mercury; if it contains more than 1 per cent. of sodium it is solid at the ordinary temperature. An alloy of lead with 35 per cent. of sodium, called **hydrone,** may also be used.

Expt. 71.—Small pieces of clean sodium are pressed one by one under the surface of dry mercury in an iron mortar. Each piece dissolves with a flash of light, poisonous fumes of mercury vapour being evolved. The amalgam is placed in a porcelain crucible in a basin of water, under an inverted jar of water. Gradual evolution of hydrogen occurs, metallic mercury being left in the crucible.

H. B. Baker and L. H. Parker (1913) found that if the amalgam and water are very pure, the action is slow, bubbles of gas appearing only at isolated points on the surface of the amalgam. If ordinary distilled water is added, the evolution of gas is accelerated, apparently owing to the presence of hydrogen peroxide in the water.

Powdered magnesium, metallic calcium, and magnesium amalgam also decompose cold water slowly.

Boiling water is decomposed readily by magnesium powder; it is also decomposed by aluminium powder, and by **copper-zinc couple**, prepared by the action of copper sulphate solution on zinc: $Zn + 2H_2O = Zn(OH)_2 + H_2$. The copper and zinc form a galvanic couple, and electrolysis occurs.

Expt. 72.—Pour a strong solution of copper sulphate over about 25 gm. of zinc dust in a 250 c.c. flask. When a deposit of copper forms, pour off the solution and fill up the flask with previously boiled water. Fit a cork and delivery tube and heat. Pure hydrogen is evolved.

Steam is decomposed by sodium, and by heated magnesium, zinc, iron, cobalt, and nickel. Copper and lead do not decompose steam.

Expt. 73.—Insert a piece of burning magnesium ribbon into a large flask in which water is boiling vigorously. The metal burns brightly in the steam, and the escaping hydrogen burns at the mouth of the flask: $Mg + H_2O = MgO + H_2$. Steam may also be passed over magnesium heated in a hard glass tube: the metal burns, but the tube usually cracks.

The decomposition of steam by red-hot iron has already been described (p. 55). Black oxide of iron, or **ferroso-ferric oxide,**

Fe_3O_4, is formed, but the decomposition of the steam is never complete. A state of **chemical equilibrium** is set up:

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2.$$

The reaction is **reversible**, and if hydrogen is passed over oxide of iron, metallic iron and steam are formed. The same mixture of hydrogen and steam results at a given temperature whether steam is passed over heated iron, or hydrogen over heated oxide of iron, the proportion of hydrogen decreasing with rise of temperature:

Ratio H_2/H_2O by volume:	20·9	5·6	2·78	2·00
Temperature:	200°	444°	860°	918°

This process is used in the **manufacture of hydrogen** (p. 707). In the **Lane process** reduced iron, from burnt pyrites or spathic iron ore (p. 503), is heated in vertical iron retorts, and steam blown through at 600–850°. The oxide of iron formed is then reduced again with water-gas (a mixture of hydrogen and carbon monoxide, formed by passing steam over red-hot coke, p. 707). The steaming and reduction processes alternate. The gas contains 98 per cent. of hydrogen, a little carbon monoxide being formed by the action of steam on carbon deposited from carbon monoxide during the reduction process: $2CO \rightleftharpoons CO_2 + C$; $C + H_2O \rightleftharpoons CO + H_2$. In the **Bergius process** iron is heated with water in a bomb to 300° under 100 atm. pressure: $Fe + H_2O \rightleftharpoons FeO + H_2$. Carbon, with a little thallium salt in the water, may be used: $C + 2H_2O = CO_2 + 2H_2$.

Special processes for the manufacture of hydrogen include the action of water on **hydrolith**, or calcium hydride:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

Hydrogenite is a mixture of 25 parts of silicon, 60 parts of caustic soda, and 20 parts of slaked lime: when ignited it burns, evolving 270–370 litres of hydrogen per kgm., and leaving sodium and calcium silicates. In the **silicol process**, powdered silicon, or an alloy of silicon with iron, is treated with a strong solution of caustic soda:

$$Si + 2NaOH + H_2O = Na_2SiO_3 \text{ (sodium silicate)} + 2H_2.$$

The manufacture of hydrogen from acetylene (p. 669), and from water-gas (p. 707), is considered later. Hydrogen is also manufactured by the electrolysis of caustic soda solution with iron or nickel electrodes, and as a by-product in alkali manufacture (p. 296).

Hydrogen from acids.—Acids are decomposed by many **metals** with liberation of hydrogen. Nitric acid does not give hydrogen unless it is very dilute and magnesium is used: all other metals give various oxides of nitrogen, ammonia, etc., but no hydrogen. The rate of liberation of hydrogen with a particular metal depends largely on what is known as the **strength of the acid,** a property which will be more exactly defined later. This must not be confused with the **concentration** of the acid.

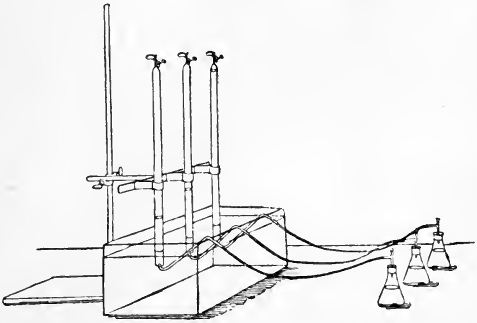


FIG. 94.—Experiment to compare Rates of Evolution of Hydrogen by Zinc from different Acids.

EXPT. 74. — Arrange three flasks with delivery tubes under graduated tubes in a pneumatic trough (Fig. 94). In each place 5 gm. of zinc, and pour in 50 c.c. of normal solutions (p. 970) of hydrochloric (36·2 gm. per litre), sulphuric (49 gm. per litre), and acetic (60 gm. per litre) acids. All these solutions contain 1 gm. of acidic hydrogen per litre. Add 1 c.c. of dilute copper sulphate to each, and after a minute has elapsed fit on the corks and observe the rate of collection of gas. The "strong" acids (hydrochloric and sulphuric) react much more rapidly than the "weak" (acetic), and hydrochloric acid more rapidly than sulphuric.

The usual **laboratory method** for the preparation of hydrogen is to act on granulated zinc with dilute sulphuric or hydrochloric acid :

$$Zn + H_2SO_4 = ZnSO_4 \text{ (zinc sulphate)} + H_2.$$
$$Zn + 2HCl = ZnCl_2 \text{ (zinc chloride)} + H_2.$$

EXPT. 75.—A tubulated bottle is one-third filled with granulated zinc and fitted with a tap-funnel and delivery tube (Fig. 95). Diluted hydrochloric acid (1 vol. of concentrated acid to 4 volumes of water), is dropped in. If very pure zinc is used, the reaction is slow, but it may be accelerated by adding a few drops of a solution of copper, nickel, or cobalt sulphate, or platinic chloride, when a zinc-metal couple is formed (p. 182). The gas is collected over water in gas jars. Before collecting the hydrogen care must be taken to

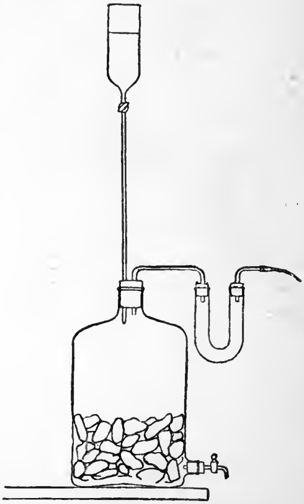


FIG. 95.—Preparation of Hydrogen.

allow all the air to be displaced from the apparatus: a little gas collected in a test-tube should burn quietly with a blue flame, and not explode, as is the case when air is still present.

The preparation may also be carried out with sulphuric acid (1 vol. of concentrated acid + 5 vols. of water), or iron turnings may be used instead of zinc: $Fe + H_2SO_4 = FeSO_4 + H_2$. The gas then has an unpleasant smell, due to hydrocarbons derived from iron carbide, Fe_3C, in the metal, and burns with a greenish flame. The solution in the flask, after filtration and slight evaporation, deposits on cooling green crystals of **ferrous sulphate** ("green vitriol"), $FeSO_4,7H_2O$.

If the solution of zinc in sulphuric acid is filtered from black particles of carbon which were contained in the metal, slightly evaporated and set aside, colourless prismatic crystals of **zinc sulphate** ("white vitriol"), $ZnSO_4,7H_2O$, separate.

Purer gas may be obtained by the action of very dilute sulphuric or hydrochloric acid on magnesium: $Mg + H_2SO_4 = MgSO_4 + H_2$; or by the action of a solution of mercuric chloride, slightly acidified with hydrochloric acid, on aluminium: $2Al + 6H_2O = 2Al(OH)_3 + 3H_2$. This gas is odourless. The liquid mercury deposited on the aluminium prevents the formation of a protective film of aluminium hydroxide.

Instead of a flask, a **Kipp's apparatus** (Fig. 96) may be used, the metal being placed in the central globe *B* and acid poured in the top funnel until the lower bulb *A* is full, and the metal covered with acid. When the tap *E* is closed evolution of gas continues until the liquid is forced by pressure partly into the upper globe, and the metal is brought out of contact with the liquid, when the action ceases.

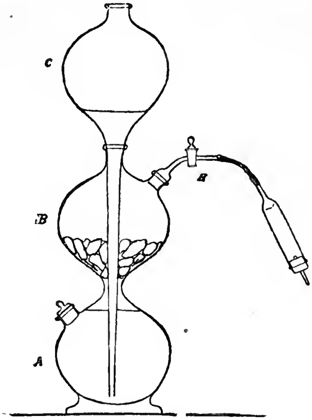


FIG. 96.—Kipp's Apparatus.

The gas from commercial zinc and acid may be **purified** by passing over red-hot copper turnings, or through wash-bottles containing a saturated solution of potassium permanganate, followed by bottles containing a 5–10 per cent. solution of silver nitrate. Impurities such as sulphuretted, phosphoretted, and arseniuretted hydrogen, oxides of nitrogen, sulphur dioxide, volatile hydrocarbons, and (if red-hot copper is used) oxygen from the air, are thus removed. A little nitrogen is left. If permanganate is used, oxygen remains, but may be removed by a solution of chromous chloride (p. 166), or by passing over heated platinised asbestos. On a large scale, bleaching powder, or a solution of bromine, is used to remove arsenic compounds from the gas.

The gas is **dried** by passing over granular calcium chloride, or sticks of caustic potash, in a tower (Fig. 97); final drying may be effected by phosphorus pentoxide alternating with plugs of glass-wool in a **U**-tube (Fig. 98). Sulphuric acid should *not* be used, as sulphur dioxide, and sulphuretted hydrogen, are formed: $H_2SO_4 + H_2 = SO_2 + 2H_2O$.

FIG. 97.—Drying Tower.

Hydrogen from alkalies.—A solution of caustic soda or potash readily dissolves zinc or aluminium on warming, with evolution of hydrogen:

$$Zn + 2KOH = K_2ZnO_2 \text{ (potassium zincate)} + H_2.$$
$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 \text{ (sodium aluminate)} + 3H_2.$$

Hydrogen prepared in this way is much purer than that from acids, and has no smell.

EXPT. 76.—Heat about 25 gm. of granulated zinc with a 30 per cent. solution of caustic soda in a flask, and collect the hydrogen. The action is more rapid if iron filings are added: these are unchanged, and probably form a galvanic couple with the zinc.

Ten gm. of aluminium turnings may also be dissolved in *dilute* caustic soda solution by warming.

Pure hydrogen is evolved from the negative electrode by the electrolysis of a warm saturated solution of barium hydroxide in a **U**-tube with platinum electrodes (Fig. 99). This is sealed to **U**-tubes containing pieces of caustic potash, followed by tubes of pure phosphorus pentoxide, to dry the gas.

If the hydrogen from the **U**-tube is first passed over heated platinised asbestos, traces of oxygen from air-leaks are burnt to water, which is taken up in the drying train. A little nitrogen is left, which is removed by passing the gas into an evacuated bulb containing **palladium** foil, previously heated in a vacuum. This readily absorbs more than 600 times its volume of hydrogen, but does not absorb nitrogen or any other gas. The residual nitrogen is pumped out of the bulb, and the latter then heated to dull redness. Perfectly pure hydrogen is evolved.

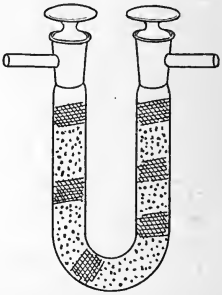


FIG. 98.—Phosphorus Pentoxide Drying Tube.

Nearly pure hydrogen may also be prepared by passing steam over sodium, or by electrolysing dilute sulphuric acid with an anode composed of a pool of zinc amalgam, which absorbs the nascent oxygen liberated at the anode:

$$Zn + O = ZnO;\ ZnO + H_2SO_4 = ZnSO_4 + H_2O.$$

The physical properties of hydrogen.—Pure hydrogen is a colourless, odourless, tasteless gas. It does not support respiration, but is not poisonous. (Impure hydrogen, containing arseniuretted hydrogen, is poisonous.) Its molecular formula is $H_2 = 2$.

Hydrogen is the lightest gas known, its normal density being 0·08987 gm. per litre. It is sparingly soluble in water, and the solubility is not greatly affected by temperature. Solubility coefficient in water: 0°, 0·0215; 10°, 0·0198; 15°, 0·0190; 20°, 0·0184.

The **spectrum** of hydrogen, obtained in a Geissler tube, consists essentially of four bright lines, although a large number of other lines are present: a red line H_α (Fraunhofer's C), 6563 Å.; a blue line, H_γ, 4340 Å.; a greenish-blue line, H_β (Fraunhofer's F), 4861 Å.; and an indigo line, H_δ, 4102 Å.

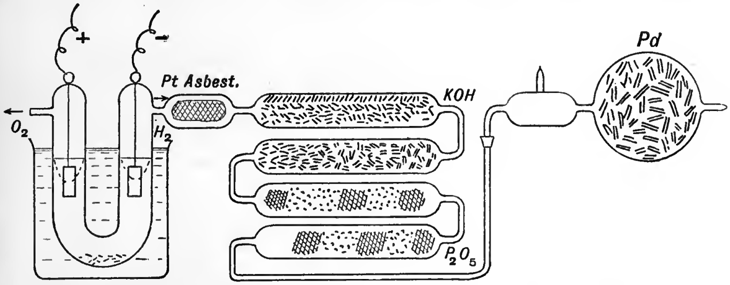


FIG. 99.—Preparation of pure Hydrogen by the Electrolysis of Barium Hydroxide solution and absorption in metallic palladium.

(1 Ångström unit = Å. = 10^{-10} metre, is the unit of wave-length, see Chap. XXXVI.)

These lines are frequently used in calibrating spectroscopes or refractometers.

Hydrogen is a good conductor of heat as compared with other gases; its conductivity is about five times that of air. Its specific heat is also abnormally high: $c_p = 2{\cdot}35$ at 0°. If a spiral of platinum wire, heated to redness by an electric current, is inserted into an inverted jar of hydrogen, the wire ceases to glow, on account of the increased loss of heat to the gas. According to Langmuir (1912), the energy-loss from a wire at high temperatures in hydrogen is greater than can be accounted for by conduction and convection:

he assumes that a slight dissociation of hydrogen into atoms occurs: $H_2 \rightleftharpoons 2H$, the reaction absorbing a large amount of heat (70–80 kg. cal. per gm. mol.).

Chemical properties of hydrogen.—Hydrogen is a **combustible gas,** burning in air or oxygen to form water (p. 165):

$$2H_2 + O_2 = 2H_2O.$$

Hydrogen also readily combines with fluorine and chlorine, and less readily with bromine, iodine, sulphur, phosphorus, nitrogen, carbon; and with a few metals, such as lithium, sodium, and calcium, it forms **hydrides,** such as NaH. The gas is not a supporter of combustion: a lighted taper passed into an inverted jar of hydrogen is extinguished.

By reason of its tendency to unite with oxygen, hydrogen acts as a **reducing agent.** Thus, if hydrogen is passed over many heated metallic oxides (copper, iron, lead), the latter are reduced to the metallic condition, and water is produced: $CuO + H_2 = Cu + H_2O$ (*cf.* Expt. 42). **Reduction** is in this case the withdrawal of oxygen. Some oxides, *e.g.*, zinc and aluminium oxides, are not reduced by hydrogen.

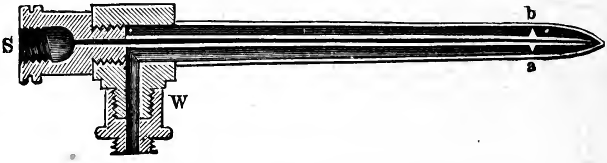


Fig. 100.—Oxy-Hydrogen Blowpipe.

Hydrogen and oxygen combine slowly at 180°, or in bright sunlight at the ordinary temperature. Explosion occurs with moist gases at 550°, but if the gases are exceedingly pure and dry they may be heated by an incandescent silver wire without explosion, though combination slowly occurs (Baker, 1902): the water produced appears to be so pure as to exert no catalytic influence on the reaction. The mixture $2H_2 + O_2$ ignites at 536° on adiabatic compression, some combination occurring before the explosion itself (**pre-flame period**): the mixture $3H_2 + O_2$ ignites at 557°, and $H_2 + 4O_2$ at 507°, respectively. There is no evidence of a minimum temperature of ignition for the mixture $H_2 + O_2$, as was formerly supposed by Falk (Dixon and Crofts, 1914).

The oxy-hydrogen and oxy-acetylene blowpipes.—When oxygen and hydrogen are supplied separately to a blowpipe jet consisting (Fig. 100) of two concentric tubes, the oxygen being inside, a blue, pointed, intensely hot flame is produced. Platinum wires readily melt in this flame, which has a temperature of about 2800°. (Carbon monoxide instead of hydrogen gives a flame temperature of about 2600°.) If the **oxy-hydrogen** (or oxy-coal gas) **flame**

impinges on a small cylinder of quicklime, which is very infusible, an intensely white light is emitted by the incandescent lime; this is called **limelight,** and is used in magic-lanterns, or for other purposes requiring brilliant illumination. In recent years, however, it has been largely replaced by the electric arc-light.

More recently, the **oxy-acetylene blowpipe** has come into use, in which acetylene gas takes the place of hydrogen, and a much hotter flame (3315°) is obtained. The flame is so hot that steam is practically completely dissociated, and the reaction is

$$C_2H_2 + O_2 = 2CO + H_2.$$

The flame is therefore strongly reducing, which makes it very suitable for **welding metals.**

In **cutting iron** or **steel** a third tube is used inside the other two (Fig. 101), and when the metal is heated by the flame to a high temperature, this inner oxygen jet is turned on. The iron itself then burns brilliantly, emitting showers of sparks, and rapidly fuses away. Since the oxygen jet is narrow, a very clean cut is produced. Plates of steel 12 in. thick can be rapidly cut through in this way.

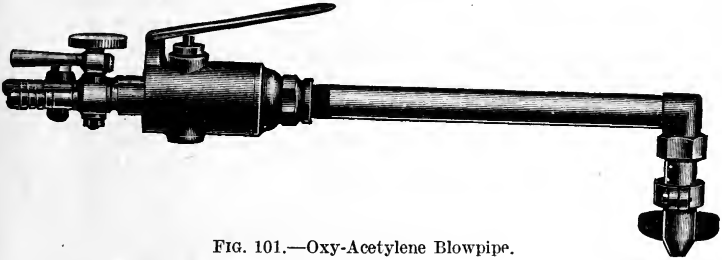


FIG. 101.—Oxy-Acetylene Blowpipe.

The acetylene and oxygen are used in the proportions 1·5 vols. of O_2 : 1 vol. of C_2H_2, the acetylene being either generated from calcium carbide and water *in situ*, or more conveniently used dissolved under pressure in acetone, soaked in a porous material contained in steel cylinders. (Compressed acetylene *gas* is liable to explode spontaneously.) The porous material is called "kapok" and consists of the seed-hairs found in the pods of a plant growing in India and Java.

Nascent hydrogen.

EXPT. 77.—If a little ferric chloride is added to a mixture of zinc and sulphuric acid which is evolving hydrogen, the ferric salt is rapidly reduced to a ferrous salt, as may be found by the appropriate tests (p. 248): $FeCl_3 + H = FeCl_2 + HCl$. No such change is produced by bubbling gaseous hydrogen through the solution.

Zinc and sulphuric acid also reduce potassium chlorate to potassium chloride, as may be found by the addition of silver nitrate.

It is supposed that the peculiar activity of the hydrogen in such cases is due to the fact that it is **nascent** (new-born), *i.e.*, in the act of liberation from its compounds, and it was generally thought that the nascent condition is due to the hydrogen being then in the state of **free atoms,** which had not time to join up to form molecules before interaction occurred. That the atomic state alone is sufficient to confer activity on an element is improbable, because the least active substances known (argon and its congeners) exist in the free state in the atomic condition. Another theory is that the hydrogen is given off under a great **pressure** at the instant of generation, and this is supported by the observation that hydrogen gas under pressure readily reduces some metallic salts (*e.g.*, $AgNO_3$) in solution. It appears, however, that the nature of the chemical action producing the hydrogen is of importance, because potassium chlorate is not reduced by sodium amalgam, which is effective in some other cases.

Zinc amalgam is often more effective than zinc alone, especially if a trace of copper salt is added, and "couples" composed of zinc with copper or iron (*cf.* p. 182) are frequently used for reduction purposes.

Uses of hydrogen.—Hydrogen finds numerous **uses** in modern industry. An air-hydrogen blowpipe is used for the **autogenous welding** of lead sheets in the making of vitriol chambers (p. 505); pure lead is used as a solder, being melted over the junction by the flame ("lead burning"). The **oxy-hydrogen** (or oxy-coalgas) **blowpipe** is used in fusing quartz in making fused silica apparatus, *e.g.*, mercury lamps, or for fusing platinum. A mixture of hydrogen and nitrogen is used in the Haber process for the **synthetic production of ammonia** (p. 543):

$$N_2 + 3H_2 \rightleftarrows 2NH_3.$$

An important use of hydrogen is in **filling balloons and airships,** 1 cu. m. of air weighs 1·29 kgm., 1 cu. m. of hydrogen weighs 0·09 kgm., so that each cu. m. of space filled with hydrogen exerts in air a lifting force of $1{\cdot}29 - 0{\cdot}09 = 1{\cdot}2$ kgm.

The first hydrogen balloon left English soil on November 25th, 1793 The balloon was used in the American Civil War of 1861, and has since been a recognised part of the equipment of an army. Dirigible airships, both on land and sea, were largely used in the war of 1914–18, including the familiar Zeppelin. The danger of fire in such cases is great, and it is proposed to replace the hydrogen by **helium** (p. 604). The hydrogen used in military balloons is usually transported in cylinders.

In recent years the importance of hydrogen has greatly increased, owing to its use in the **hardening of fats**, *e.g.*, in the preparation of **margarine** from oils by treating the latter with pure hydrogen in presence of finely-divided nickel, when the unsaturated liquid fats take up hydrogen (p. 1005).

Diffusion of gases.—The hydrogen contained in an open *inverted* jar rapidly diffuses out, and air enters; this movement takes place in opposition to gravity. Döbereiner in 1823 found that hydrogen confined over water in a cracked flask escaped into the surrounding air, the water rising in the neck of the flask. Graham showed that as the hydrogen escaped, air entered the flask, and since the pressure inside is reduced, it follows that the hydrogen diffuses out more rapidly than air diffuses in. If the flask was covered with a bell-jar of hydrogen, no change in the level of water occurred.

Graham devised a more convenient apparatus for measuring the **rates of diffusion of gases,** consisting of a glass tube closed at one end with a thin plug of plaster of Paris. This tube is filled with mercury, which is then displaced by hydrogen (Fig. 102). The mercury rises in the tube, and the latter may be sunk in a jar of mercury so as to keep the level constant. After a certain time all the hydrogen diffuses out, and the tube contains only air which has diffused inwards. No further change of volume then occurs. If the volume of residual air is measured, it gives the volume diffusing in the same time as the whole of the hydrogen originally contained in the tube. The inverse ratio of these *volumes* gives the ratio of the *times* required for the diffusion of equal volumes. In this way Graham found the following table, the velocity of diffusion being the ratio of volumes diffusing in equal times :—

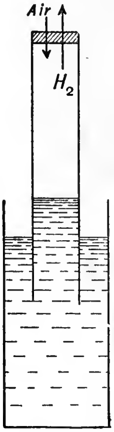


FIG. 102. Graham's Diffusion Apparatus.

Gas.	**Density** (Air = 1)	$\frac{1}{\sqrt{\text{Density}}}$	**Velocity of diffusion** (Air = 1).
H_2	0·069	3·78	3·83
CH_4	0·559	1·34	1·34
N_2	0·971	1·015	1·014
O_2	1·1056	0·951	0·950
CO_2	1·529	0·809	0·812

Thus, the **velocity of diffusion of a gas is inversely proportional to the square root of its density.** This is known as **Graham's law** (1833).

EXAMPLE.—One hundred c.c. of hydrogen are confined in a diffusion tube exposed to air. When change of volume ceases, what volume of air will be left in the tube ?

The volumes diffusing are inversely proportional to the densities,

$$\therefore \frac{\text{volume of hydrogen}}{\text{volume of air}} = \frac{\sqrt{1{\cdot}293}}{\sqrt{0{\cdot}09}}$$

$$\therefore \text{ vol. of air} = 100 \times \frac{\sqrt{0{\cdot}09}}{\sqrt{1{\cdot}293}} = 26{\cdot}4 \text{ c.c.}$$

EXPT. 78.—The phenomenon of diffusion may be illustrated by the apparatus shown in Fig. 103. A porous clay pot, such as is used in batteries, is fitted by a rubber bung to a tube passing into a Woulfe's bottle containing coloured water, as shown. Dipping into the coloured water is a glass tube drawn out to a jet above. If a large beaker of hydrogen is inverted over the clay pot, hydrogen diffuses into the latter more rapidly than air passes out, and the increase of pressure causes the water to issue from the jet in the form of a fountain. If the beaker is now removed, hydrogen inside the porous pot diffuses out into the air more rapidly than air enters, so that the pressure is reduced. Coloured water thus rises in the vertical tube attached to the porous pot.

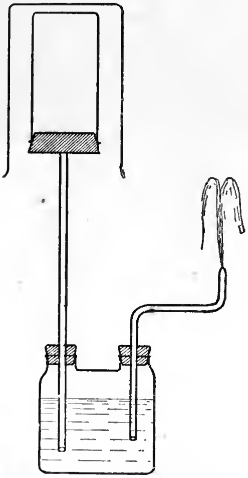


FIG. 103.—Experiment on Diffusion.

Liquid and solid hydrogen.—The first serious attempt to liquefy hydrogen was made by two Polish investigators, Wroblewski and Olszewski, in 1884. They cooled the gas to − 183°, and allowed it to expand from 100 atm. pressure, obtaining evidence of liquefaction, but getting no liquid in bulk. The latter was first obtained by Dewar in 1895, at the Royal Institution in London. By compressing hydrogen to 200 atm., cooling it to − 200°, and expanding it through a valve, he obtained a colourless liquid, readily boiling off. This was **liquid hydrogen**. Olszewski in 1895 found that the critical temperature of hydrogen is about − 234° (the accurate value is − 234·5°; the critical pressure is 20 atm.), and that the slight heating effect produced by expansion through a valve at the ordinary temperature (Joule-Kelvin effect) changes, on cooling to − 80·5° at 113 atm., into a **cooling effect**. This **inversion point** makes it necessary in the liquefaction of hydrogen first to cool the gas strongly before expansion.

Liquid hydrogen is a colourless, transparent liquid, with the very small density of 0·07105 at − 252·8° and 745·52 mm. It boils at − 252·7°. By rapidly evaporating the liquid under reduced pressure in a tube immersed in liquid hydrogen in a double Dewar vessel (Fig. 104), its temperature is reduced to − 259°, when it freezes to a colourless, transparent **solid** or a white, snow-like mass. At the temperature of liquid hydrogen all other gases except helium are frozen to solids which at the extreme cold show practically no vapour pressure.

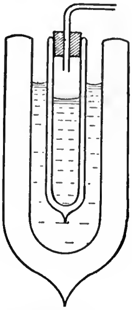


FIG. 104. Preparation of Solid Hydrogen.

If a Geissler tube is attached to a bulb containing charcoal, and the latter dipped into liquid hydrogen, the vacuum in the Geissler tube becomes so intense that no electrical discharge will pass even with a powerful coil (Fig. 105).

If a barometer tube filled with air is inverted in mercury, and the bent closed end dipped first into liquid air and then into liquid hydrogen, the air in the tube becomes solid, and the mercury rises to a height corresponding with an almost perfect vacuum.

If liquid hydrogen is poured into an ordinary test-tube, a white coating of ice at once covers the outside. From this, drops of liquid air are seen to fall.

Liquid hydrogen may be prepared in the modification of Travers' apparatus devised by Nernst (Fig. 106). Compressed hydrogen from a cylinder or compressor enters the apparatus through the copper coil, *A*, and passes through an extension, *A′*, of the coil immersed in liquid air in a large Dewar vessel. It then passes, after cooling in this way, through an extension of the coil, *A″*, composed of two coils in parallel inside a small Dewar tube completely enclosed in a brass vessel, *B*. At the end of this coil is an expansion valve, *V*, similar to those used in the Linde apparatus, which is operated from outside. In the tube *A″* the previously cooled gas is liquefied by the cold expanded gas from the valve sweeping over the coil, and liquid hydrogen collects in the inner Dewar vessel. The cold hydrogen gas passes out through a copper coil, *C*, wound in contact with the coil *A*, and takes heat from the incoming hydrogen in the latter, escaping into the free air, or to the compressor, only slightly below atmospheric temperature. The liquid air boiling in the outer Dewar

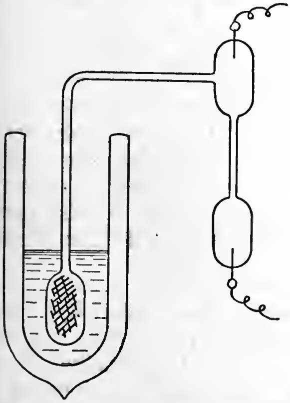


FIG. 105.—Experiment to show the very low temperature of Liquid Hydrogen.

vessel gives off cold air, which passes out through a copper coil, *D*, wound between the two coils *A* and *C*, and also takes up heat from the incoming hydrogen. The brass vessel, *B*, is in two parts, screwed together, to permit of the inner Dewar tube being inserted. 300–400 c.c. of liquid hydrogen are obtained per hour, with a gas velocity of 2–3 c.c. per second, and the use of about 300 c.c. of liquid air.

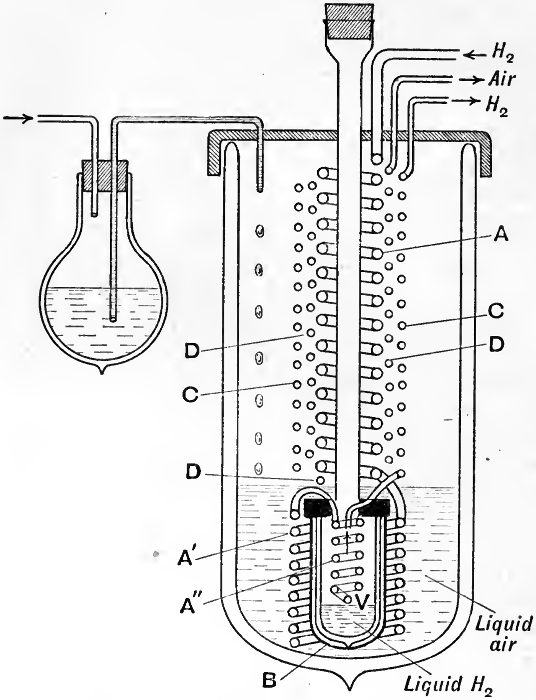


FIG. 106.—Preparation of Liquid Hydrogen.

The occlusion of hydrogen by metals.—Deville observed that platinum and iron become permeable to hydrogen at a red heat, and thence concluded that "metals and alloys have a certain porosity." Thomas Graham (1866–8) showed, however, that the penetration cannot be due to the porosity of the metal, since hydrogen is practically the only gas which exhibits the effect.

Graham filled a platinum bulb with hydrogen, and heated it in air. In half an hour 97 per cent. of the hydrogen had passed out, but no air entered, and a partial vacuum was produced inside the tube. Five hundred c.c. of hydrogen passed per sq. m. per minute through a platinum tube 1·1 mm. thick. Through a similar palladium tube the hydrogen began to escape at 100° ; at a red heat 3993·2 c.c. of gas passed out per sq. m. per minute. No other gas, except ether vapour, penetrated the metal. Palladium in a glass tube was exposed to hydrogen at 90–97° for three hours, and allowed to cool in the gas, for ninety minutes. When the tube was heated by a flame, and the gas pumped off, the metal yielded 643 times its volume of gas. Upwards of 500 vols. of gas were given out when evacuation was carried out at 245°. The surface of the palladium became roughened, and the metal was rendered brittle. Iron absorbs 4 vols. of carbon monoxide, and a piece of meteoric iron gave out 3 vols. of gas, 86 per cent. of which was hydrogen —" the hydrogen of the stars."

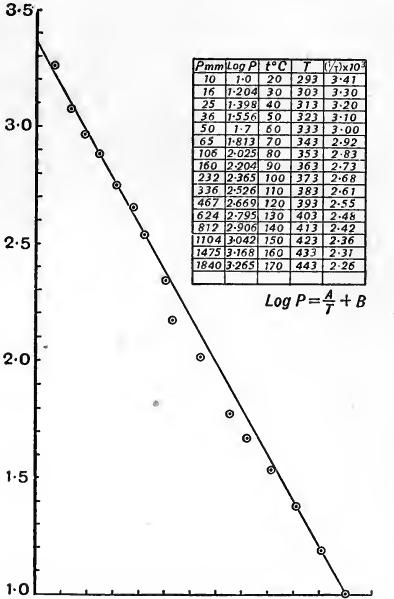
Graham said that: "the whole phenomenon appears to be consistent with the solution of liquid hydrogen in the metal . . . It may be allowed to speak of this as the power to occlude (to shut up) hydrogen, and the result as the **occlusion** of hydrogen by platinum." In 1868 he modified his view, advancing the extraordinary hypothesis that hydrogen was the vapour of an exceedingly volatile **metal, hydrogenium**: "The idea forces itself on the mind that palladium with its occluded hydrogen is simply an *alloy* of this volatile metal, in which the volatility of one element is restrained by its union with the other, and which owes its metallic aspect equally to both constituents." This hypothesis was exploded when solid hydrogen was shown to be a transparent, glassy solid, entirely devoid of metallic properties.

Palladium charged with hydrogen is a strong **reducing agent**: it precipitates mercury from mercuric chloride solution, gives up hydrogen to chlorine and iodine in the dark, and reduces ferric to ferrous salts. Colloidal palladium takes up 2950 vols. of hydrogen.

Expt. 79.—The occlusion of hydrogen by palladium is exhibited by immersing two strips of palladium foil in dilute sulphuric acid, and using them as electrodes. Oxygen is evolved from the anode, but no gas is evolved from the cathode until the metal becomes charged with hydrogen, when a stream of bubbles begins to come off. If the current is switched off, gas continues to come off slowly from the cathode, showing that the metal had become *supersaturated* with hydrogen. If the current is then at once reversed, no gas comes from either electrode for a time. The oxygen is combining with the occluded hydrogen in the one electrode, and hydrogen is being occluded in the other. After a time gas comes off from both electrodes.

Troost and Hautefeuille (1874) pumped off the gas from the palladium at a given temperature, and measured the pressures during its removal. The first portions of gas came off fairly readily, but when 600 vols. of hydrogen were left to 1 vol. of palladium, the pressure became constant, and the rest of the gas came off at this constant pressure. The phenomenon resembles the dehydration of a salt containing water of crystallisation (p. 204), and hence these observers concluded that a definite **hydride of palladium** was present. The same relations were observed at different temperatures, which confirms the hypothesis.

The density of palladium is 12, hence the ratio of the weights of palladium and hydrogen in the metal which has occluded 600 vols. of hydrogen is $12 : 600 \times 0{\cdot}00009 = 12 : 0{\cdot}054$. The atomic weight of Pd is 106, hence the ratio of the atoms in palladium saturated with hydrogen is $\frac{12}{106} : 0{\cdot}054 = 2{\cdot}03 : 1$, which is very near the formula Pd_2H. The author found (1919) that the logarithms of the dissociation pressures found by Troost and Hautefeuille when plotted against the reciprocals of the absolute temperatures gave very nearly a straight line (Fig. 107). From the slope of this line the heat of occlusion of 1 gm. of hydrogen in palladium was found to be 4568 gm. cal. The value measured calorimetrically by Mond, Ramsay, and Shields (1897) was 4672 gm. cal., in satisfactory agreement.



Pmm	Log P	t°C	T	$(1/T) \times 10^3$
10	1·0	20	293	3·41
16	1·204	30	303	3·30
25	1·398	40	313	3·20
36	1·556	50	323	3·10
50	1·7	60	333	3·00
65	1·813	70	343	2·92
106	2·025	80	353	2·83
160	2·204	90	363	2·73
232	2·365	100	373	2·68
336	2·526	110	383	2·61
467	2·669	120	393	2·55
624	2·795	130	403	2·48
812	2·906	140	413	2·42
1104	3·042	150	423	2·36
1475	3·168	160	433	2·31
1840	3·265	170	443	2·26

$$\text{Log } P = \frac{A}{T} + B$$

FIG. 107.—Dissociation Pressures of Hydrogen in Palladium.

Roozeboom and Hoitsema (1895) repeated the investigations of the two French chemists, but found that the pressure curves in the dissociation of the "palladium hydride," at temperatures between 0° and 190°, consisted of *three* parts (Fig. 108): two rapidly ascending portions, joined by a nearly horizontal but slowly rising middle portion. At higher temperatures the flat part becomes appreciably shorter. It is less flat if palladium black is used instead of foil. The dotted curves give the results of Troost and Hautefeuille. The shapes of the curves were considered to speak against the existence of a definite compound; with certain reservations Roozeboom and Hoitsema thought they indicated the formation of a **solid solution.** The flat part, where the pressure is practically constant, indicates that *two* solid solutions must be present.

Thus, since the pressure depends only on the temperature, the degrees of freedom = 1; the number of components = 2, ∴ number of phases = 3, *i.e.*, gas + 2 solids. (*Cf.* p. 106.)

Roozeboom and Hoitsema pointed out that their hydrogen contained a little nitrogen, which would explain the upward slope of the curves: they did not consider their experiments sufficient to decide the question.

Holt, Edgar, and Firth in 1913 call the occlusion of hydrogen by palladium **sorption,** since they concluded that the hydrogen exists partly as a condensed layer on the surface, and partly dissolved in the interior of the metal. The second part is not usually homogeneously distributed throughout the metal.

They found that palladium exists in two forms, an **active form,** which readily absorbs hydrogen, and an **inactive form,** which does not. Inactive palladium becomes active as a result of: (*a*) oxidation by heating in air and reduction of the oxide film in hydrogen; (*b*) heating to 400° in hydrogen, followed by cooling in the latter; (*c*) heating to 400° *in vacuo*; the hydrogen must then be admitted as soon as cold, as the metal so activated soon loses its activity. In all cases, **heating** is necessary for the activation, hence the active form of the metal is probably an unstable variety, whilst the stable crystalline form is inactive.

The absorption of gas is at first rapid, then becomes increasingly slower. This suggests that there is at first a condensation of gas on the surface; when this becomes saturated there is a slow diffusion of hydrogen through the mass of the metal.

The rate of diffusion of hydrogen through palladium 0·3 mm. thick was 3288 c.c. per sq. m. per minute at 200°, and 5570 c.c. at 476°.

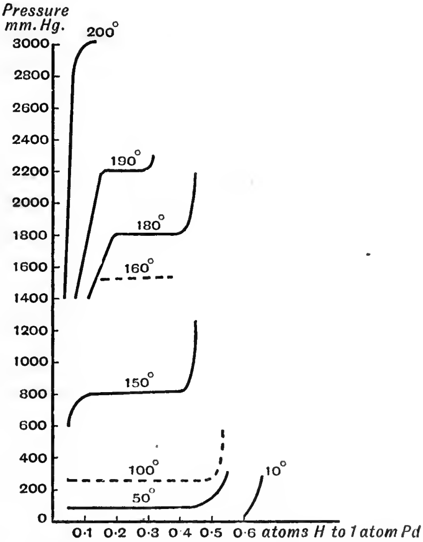


FIG. 108.—Palladium and Hydrogen Curves.

By pumping out a palladium tube saturated with hydrogen and surrounded with the gas, the pressure inside was reduced to zero at the ordinary temperature, whilst the pressure on the other side was 10·4 mm. At 140°, with two pumps working equally on both sides, the outer surface of the tube then lost 208 c.c. of gas, and the inside only 12 c.c. The hydrogen therefore appears not to be homogeneously distributed throughout the metal. The surface layer is easily removed by pumping; the gas in the interior is much more firmly held.

A. W. Porter (1918) has pointed out that different phenomena may be confused under the name "occlusion": (*a*) formation of a chemical compound; (*b*) simple solid solution, with or without chemical combination; (*c*) solid solution in contiguous phases (Hoitsema); (*d*) surface condensation under molecular forces, especially in pores; (*e*) inclusion of bubbles of gas.

Most metals in the finely-divided condition absorb small quantities of hydrogen, and metals prepared by electrolysis sometimes contain occluded hydrogen.

Catalytic combustion.—Although oxygen and hydrogen do not combine at the ordinary temperature, a jet of hydrogen is inflamed if directed on a little platinum sponge, obtained by heating ammonium chloroplatinate [$(NH_4)_2PtCl_6$]. The same effect is produced by a bundle of fine platinum wires, which become red-hot and then kindle the hydrogen (Döbereiner, 1823). This action is not shown by metals such as iron or copper, and in this case, therefore, the platinum exerts a **catalytic action** (p. 166).

Döbereiner's lamp consists (Fig. 109) of a small hydrogen generator, composed of a bell-jar immersed in dilute sulphuric acid with a stopcock and jet at the top. A piece of zinc hangs inside, and the gas generated displaces the acid until it is no longer in contact with the zinc, when action ceases. Opposite the jet is a sponge of fine platinum wire enclosed in a brass tube, and when the tap is opened the stream of hydrogen ignites. The activity of the platinum rapidly falls off, but it may be renewed by boiling the metal in nitric acid, when impurities from the hydrogen, which cause the loss of activity, are removed.

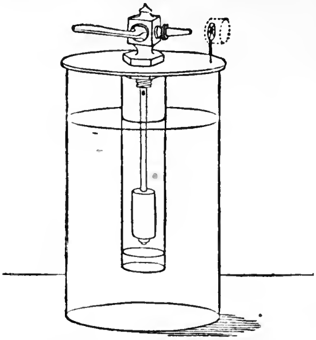


FIG. 109.—Döbereiner's Lamp.

Faraday (1833) observed that the combination of a mixture of hydrogen and oxygen can also be brought about by a piece of *clean* platinum foil—in some cases the gas explodes. There are two theories to account for this **catalytic activity of platinum** in bringing about the union of hydrogen and oxygen:

(1) **Faraday** considered that both the gases formed a **condensed film** on the metal surface—they might even be liquid. This was the result of the action of surface-forces. Under the high pressure existing in this film the gases entered into reaction. It is in fact known that pressure enhances the activity of gases. Thus, Beketoff found that hydrogen gas displaces silver and mercury from solutions of their salts under 100 atm. pressure.

(2) **De la Rive** (1834), on the contrary, believed that **chemical compounds,** unstable oxides, are formed as superficial layers on the metal.

These react with the hydrogen in a cyclic manner, the metal being alternately oxidised and reduced : $2Pt + O_2 = 2PtO$; $2PtO + 2H_2 = 2Pt + 2H_2O$. There is some evidence for the formation of superficial oxide films. Both theories persist to the present day, and it is probable that both effects, the physical and the chemical, play a part in the action.

EXERCISES ON CHAPTER XI

1. Describe briefly four typical methods for preparing hydrogen. How is the pure gas obtained ?

2. By what metals, and under what conditions, is water decomposed with liberation of hydrogen ? Describe the commercial processes for the preparation of hydrogen from water and iron.

3. For what purposes is hydrogen used ? Describe the construction and use of the oxy-acetylene blowpipe.

4. What do you understand by "nascent hydrogen" ? Give two experiments to show how nascent hydrogen differs from ordinary hydrogen.

5. State Graham's law of diffusion, and describe an experiment to show that hydrogen diffuses more rapidly than air. How many c.c. of hydrogen will pass through a porous plug in the same time as 1 c.c. of air ?

6. Describe briefly the methods used in the preparation of liquid and solid hydrogen.

7. Give an account of the absorption of hydrogen by metals. What theories have been advanced as to the nature of the products ?

8. Describe an experiment to illustrate the catalytic effect of platinum in the combination of hydrogen and oxygen. What explanations of the action have been given ?

CHAPTER XII

WATER

The physical properties of water.—Water exists in three states of aggregation: solid (**ice**), liquid (**water**), and vapour (**steam**). What is ordinarily called "steam" is not true water vapour, which is invisible, but a mist of small droplets of liquid water.

EXPT. 80.—Boil some water in a flask fitted with a short bent tube. A cloud of "steam" issues from the tube, but the interior of the flask, which is filled with water vapour, is quite clear. If a Bunsen flame is held below the delivery tube, the mist disappears. A short distance from the tube is also seen to be clear in the first part of the experiment. This consists of vapour which has not cooled to the condensing point.

Liquid water possesses a faint though distinct bluish-green colour, which is seen when light is passed through a tube of water 2 m. long, closed at the ends with pieces of plate glass. Ice also shows the same colour in large masses, as in the crevices of glaciers or ice-floes. The deep blue colour of certain clear lakes, however, appears to be due to light scattered from fine particles of solid matter in suspension (*cf.* p. 7).

Liquid water is only slightly compressible; between 1 and 25 atm. an increase of pressure of 1 atm. reduces the volume by only 5 parts in 100,000. The expansion of water by heat is peculiar. From 0° to 3·98°, the liquid *contracts*; beyond 3·98° it expands. Thus, at 3·98° water is in a state of **maximum density,** and then expands either on heating or on cooling. Owing to this property, exposed water freezes only on the surface; the water sinks as it reaches 3·98°, and forms a heavier layer beneath the upper crust of ice, through which heat is only very slowly transmitted.

The volume of 1 kgm. of water at 4° weighed *in vacuo* is defined as the **standard litre**; it occupies 1000·027 c.c. The volume of 1 kgm. of water at 15°, weighed *in vacuo*, is **Mohr's litre**; it occupies 1000·91 c.c.

The density of ice is 0·9160 at 0°; it therefore floats on water, and water expands on freezing. Water pipes are burst on freezing;

the result is obvious when a thaw sets in. Cast-iron bottles filled with water and closed with screw plugs are burst when immersed in a freezing mixture.

The **densities of water,** referred to the weight of one-thousandth of a standard litre at 4° as unity, are as follows :

DENSITIES OF WATER.

0°	0·99987	10°	0·99973	− 5° (supercooled)	0·99930
4°	1·00000	20°	0·99823	150°	0·917
8°	0·99988	100°	0·9584	250°	0·79

The amount of heat required to raise the temperature of 1 gm. of water from $14\frac{1}{2}°$ to $15\frac{1}{2}°$, *i.e.*, through 1°, is called the **calorie.** This varies slightly with the temperature of the water; thus at 0° and 100° it is slightly greater than at 15°. The corresponding amount for 1 kilogram of water is the **kilogram calorie :** 1 kgm. cal. = 1000 cal. This heat may be generated by stirring the water, and the number of units of work spent in generating 1 calorie is called the **mechanical equivalent of heat.** Expressed in ergs this is $4·184 \times 10^7$ ergs per gm. cal. (1 erg is twice the **energy** possessed by a mass of 1 gram moving with a speed of 1 cm. per second.) This number, first determined by Joule, is denoted by J.

The number of calories required to raise the temperature of 1 gram of a substance through 1° under specified conditions is called the **specific heat** of the substance. Thus, the specific heat of ice is 0·502.

When ice is converted into water a considerable absorption of heat takes place, although the temperature remains constant at 0°. This heat, which amounts to 79·77 cal. per gram of ice, is called the **latent heat of fusion** of ice (or the **latent heat of water**). Other pure substances possess characteristic latent heats. Similarly, when water at its boiling point is converted into steam a large absorption of heat occurs. For 1 gm. this amounts to 538 cal., and this is called the **latent heat of evaporation** of water (or the **latent heat of steam**). In the reverse changes of solidification or liquefaction exactly the same quantities of heat are *evolved.*

The **vapour density** of water just above the boiling point is slightly greater than that corresponding with the formula H_2O. The presence of double molecules, **dihydrol** $(H_2O)_2$, is sometimes assumed to explain this. Liquid water is also assumed to consist of dihydrol and **hydrol** (H_2O) molecules in equilibrium: $2H_2O \rightleftharpoons (H_2O)_2$. To explain the anomalous expansion below 3·98°, the presence of **trihydrol,** $(H_2O)_3$, molecules is assumed, which are formed from hydrol by expansion. Ice would then consist largely of trihydrol, which is also present in cold water. Although there is evidence that liquid water is **associated,** or contains complex molecules in equilibrium, the existence of these dihydrol and trihydrol molecules is hypothetical. The case is further complicated by the existence of four or five different **varieties of ice** formed from ordinary ice under high pressures. These are all denser than water, but different varieties lighter than water are also indicated.

The **vapour pressure of water** has already been considered (p. 74): the vapour pressures of ice are slightly less than those of supercooled liquid water at the same temperatures. Water is readily cooled below 0° if kept at rest, and is then **supercooled.** In contact with ice, or if violently agitated, it freezes, and the temperature rises to 0°. Similarly, drops of water floating in oil are readily heated much above 100° without vaporising, and are then said to be **superheated.** (" Superheated steam " is merely steam which has been raised above 100°, or the temperature of saturation, by passing through heated tubes.)

The **solvent properties** of water have already been described. Some chemists are of the opinion that dissolved salts are in some way " loosely combined " with the water to form unstable **hydrates** : *e.g.*, $NaCl + xH_2O \rightleftharpoons NaCl,xH_2O$. It is supposed that, as a result of the removal of hydrol molecules, further dissociation of dihydrol and trihydrol occurs, leading to the changes of volume which take place on solution. This **hydrate theory of solution** has led to no unequivocal results, and although quite obviously plausible, it is supported by no very cogent experimental evidence.

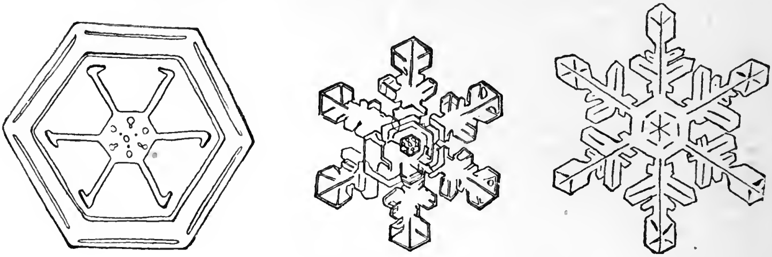


FIG. 110.—Ice Crystals.

Ice crystallises in the hexagonal (six-sided) system. Beautiful hexagonal crystals are seen (Fig. 110) when snowflakes are examined on a cold slide under the microscope, and the crystalline form of ice is also observed when a beam of light from a lantern is passed through a slab of ice, which slowly melts. The bubbles in ice are composed of air which was dissolved in the water, and is liberated on freezing. In making clear ice, the freezing is carried out slowly, with agitation, so that the air bubbles have an opportunity to escape. Rectangular tanks filled with water are immersed in a large tank through which a cold solution of calcium chloride ("brine"), which does not freeze until $-30°$, is circulated from a refrigerating machine (p. 547).

Efflorescence.—Many salts form definite solid chemical compounds with water, called **hydrates.** Thus, if water is poured on white anhydrous copper sulphate, the salt at once becomes blue, and heat is evolved. If a hot solution of copper sulphate in water is cooled, deep blue crystals of the hydrate, $CuSO_4,5H_2O$, called blue vitriol, separate out. If these are exposed to dry air in a desiccator over sulphuric acid, they fall to a white powder of the monohydrate, $CuSO_4,H_2O$, which again becomes blue when moistened with water.

Some crystalline hydrates lose water of crystallisation, and fall to powder on exposure to air. This change is called **efflorescence.** The loss of water as vapour on exposure to air shows that there must be a certain pressure of water vapour over the salt, and this is confirmed by passing a crystal of washing soda, or Glauber's salt, above the mercury in a barometer tube, when the mercury falls slightly. The **vapour pressure** of a salt hydrate may be measured in this way. It is found to be constant at a given temperature, and to increase with the temperature, in the same way as the vapour pressure of a liquid (p. 105).

In the system just described we have two components, viz., the anhydrous salt, and water. Since the vapour pressure depends only on the temperature, there is only one degree of freedom (p. 106); hence the Phase Rule, $P + F = C + 2$, shows that the number of phases is: $2 + 2 - 1 = 3$. These phases are water vapour and *two* solids. One solid is the original hydrated salt; the second is the anhydrous salt, if this is produced directly by loss of water, as is the case with Glauber's salt: $Na_2SO_4,10H_2O = Na_2SO_4 + 10H_2O$ (vap.), or a lower hydrate, as is the case with copper sulphate:

$$CuSO_4,5H_2O = CuSO_4,3H_2O + 2H_2O.$$

When, at the ordinary temperature, the vapour pressure of water above the hydrated salt is greater than the partial pressure of moisture in the atmosphere, the salt will lose water continuously on exposure to air, and will effloresce. If, on the other hand, the pressure over the salt is not greatly different from that of atmospheric moisture, the crystals of the salt will be stable on exposure to air. Thus, blue vitriol does not effloresce on exposure to air, since the vapour pressure over its crystals at 25° is only 7·4 mm., whilst the partial pressure of atmospheric moisture, which is usually about two-thirds the saturation pressure at the given temperature, would be 15 mm. If the vapour pressure over the hydrate is very small, it may even absorb moisture from the air. Thus, ordinary granular calcium chloride used for drying gases is $CaCl_2,2H_2O$. This has a very small vapour pressure, and absorbs moisture from gases, forming $CaCl_2,6H_2O$, until only an exceedingly small amount of moisture is left in the gas.

Vapour pressures of hydrates.—The existence of a definite vapour pressure over a hydrated salt, as compared with the variable pressure over a solution, when water is abstracted from the material, enables us to distinguish between the two cases. A mechanical mixture of liquid water with a solid may be distinguished from the two cases just mentioned by the fact that its vapour pressure is that of pure water, provided a solution is not formed. A hydrate containing hygroscopic moisture, *i.e.*, water in excess of its combined amount, will show a vapour pressure equal to that of its saturated solution, until all the excess of moisture has been lost ; the pressure will then drop abruptly to that of the definite solid hydrate.

When the excess of moisture has evaporated, the definite hydrate is left, say $CuSO_4,5H_2O$, and the pressure falls abruptly to *A* (Fig. 102). Dissociation of this hydrate then begins: $CuSO_4,5H_2O \rightleftarrows CuSO_4,3H_2O + 2H_2O$, and the next lower hydrate, say $CuSO_4,3H_2O$, is formed. The system composed of the two solid hydrates, $CuSO_4,5H_2O$ and $CuSO_4,3H_2O$, has, in accordance with the Phase Rule, a definite pressure. With continued abstraction of water, all the higher hydrate, $CuSO_4,5H_2O$, is converted into the lower hydrate, $CuSO_4,3H_2O$. When this occurs, the pressure again falls abruptly to a lower value, represented by *C*.

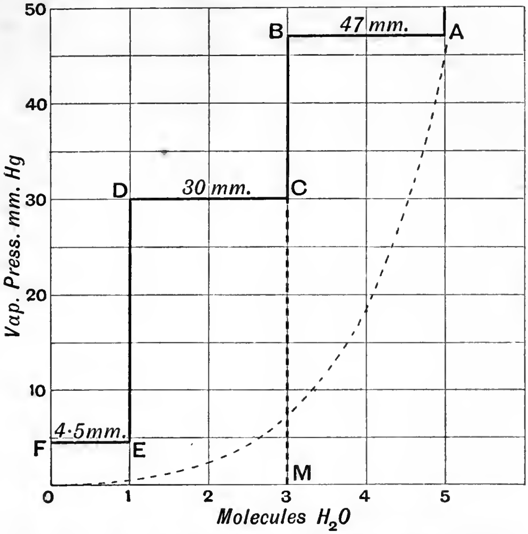


FIG. 111.—Vapour Pressure Curves for Dissociation of a series of Hydrates of Copper Sulphate at 50°.

Dissociation into the lowest hydrate, $CuSO_4,H_2O$, now begins: $CuSO_4,3H_2O \rightleftarrows CuSO_4,H_2O + 2H_2O$. This hydrate has a very small vapour pressure, but gives off moisture in a desiccator over phosphorus pentoxide, forming the anhydrous salt. Until all the trihydrate is converted into the monohydrate, the pressure remains constant. It falls sharply to a very low value, *E*, when the solid is converted entirely into monohydrate, remains at this low pressure until all the water is removed, and then falls to zero over the anhydrous salt: $CuSO_4,H_2O \rightleftharpoons CuSO_4 + H_2O$.

By analysing the solid when the sudden drops of pressure occur, say at *C*, the composition of the lower hydrates may be found.

The dotted curve *AO* represents the vapour pressure of a solid solution (*e.g.*, jelly).

Natural waters.—Water as it occurs in Nature contains various impurities. The following division of **natural waters** is convenient: (1) **rain water,** (2) **river water,** (3) **spring,** or **deep well, water,** (4) **sea water,** and (5) **mineral waters.**

The **impurities in natural water** are of two kinds: (1) **suspended** impurities, both mineral and organic; (2) **dissolved** impurities, both **solids** (mineral and organic), and **gases.** These are present in amounts varying considerably with the particular source of the water.

Rain water always contains impurities, especially if it is deposited in the neighbourhood of towns where coal is burnt. Dissolved atmospheric gases (oxygen, nitrogen, carbon dioxide), and sodium chloride, derived from sea-spray carried inland by winds, are invariably present. Nitrous and nitric acids, produced by electrical discharges (lightning), are nearly always present in the forms of ammonium nitrate and nitrite, and sometimes free ammonia occurs. In the vicinity of towns, sulphuric acid, from the sulphur dioxide formed by the combustion of coal (which contains iron pyrites, FeS_2), is present. The suspended impurities, chiefly soot from fuel smoke, are contained in larger amounts in rain falling near towns, and the water must then be allowed to settle before use. The free sulphuric acid may be neutralised by adding a little lime-water, or by allowing the water to stand over limestone. Melted snow contains similar impurities.

River water is rain water which has percolated through the surface-soil, and taken up salts, organic matter, and suspended matter such as clay. The dissolved matter is especially marked when the water has passed through limestone or calcareous soil (*i.e.*, soil rich in calcium carbonate), because the carbonic acid present in the rain, produced from atmospheric carbon dioxide: $CO_2 + H_2O \rightleftharpoons H_2CO_3$, dissolves the carbonates of calcium and magnesium, forming soluble bicarbonates. These are unstable, and are readily decomposed on boiling the water, with precipitation of the insoluble carbonates and evolution of carbon dioxide:

$$CaCO_3 + H_2CO_3 \rightleftharpoons CaH_2(CO_3)_2; \text{ or } MgCO_3 + H_2CO_3 \rightleftharpoons MgH_2(CO_3)_2.$$

Expt. 81.—Pass a stream of carbon dioxide (washed free from acid spray by passing through a wash-bottle containing water) into lime-water. The latter at first becomes turbid, owing to the formation of insoluble **calcium carbonate**: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$. On continued passage of the gas, the precipitate redissolves, producing **calcium bicarbonate**: $CaH_2(CO_3)_2$, or $CaO,2CO_2 + H_2O$ (*i.e.*, a substance containing *twice* as much CO_2, for the same weight of lime, as the carbonate, CaO,CO_2). On boiling the clear liquid, it again becomes turbid, and calcium carbonate is precipitated. The reaction is therefore reversible: $CaCO_3 + H_2O + CO_2 \rightleftarrows CaH_2(CO_3)_2$. If an equal volume of lime-water is added to the clear bicarbonate solution, turbidity is produced, and nearly insoluble calcium carbonate precipitated: $CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$ (or, omitting water: $CaO,2CO_2 + CaO = 2CaO,CO_2$). The filtrate is practically free from calcium salts.

The presence of the bicarbonates of calcium and magnesium produces what is called **temporary hardness** of water, *i.e.*, such water destroys soap without producing a lather, but is "softened" by boiling.

Hard and soft waters.—The different varieties of hard **soap** consist of the sodium salts of three organic acids, derived from fats: **Oleic acid,** $C_{17}H_{33}{\cdot}CO_2H$; **palmitic acid,** $C_{15}H_{31}{\cdot}CO_2H$; **stearic acid,** $C_{17}H_{35}{\cdot}CO_2H$; sodium oleate, $C_{17}H_{33}{\cdot}CO_2Na$; sodium palmitate, $C_{15}H_{31}{\cdot}CO_2Na$; sodium stearate, $C_{17}H_{35}{\cdot}CO_2Na$ ("soft soap" consists of the *potassium* salts of these acids).

These salts are soluble in water, but are slightly decomposed by the latter, giving caustic soda:

$$C_{15}H_{31}{\cdot}CO_2Na + H_2O \rightleftarrows C_{15}H_{31}{\cdot}CO_2H + NaOH.$$

This process of decomposition of a salt by water, with production of free acid and base, is called **hydrolysis.** The reaction is reversible; in very dilute solutions, with a large excess of water, the hydrolysis may be nearly complete, whilst in concentrated solutions the extent of hydrolysis is small. In consequence, the actual percentage of caustic soda in the solution is nearly the same for all dilutions; it is automatically regulated, and the soap does not produce enough caustic soda to injure the skin. The soap in addition lowers the surface tension of water fairly considerably, so that the soapy water readily froths, and particles of dirt tend to accumulate in the soapy liquid. The detergent action of soap is thus an instance of separation by surface tension effects (p. 10).

Expt. 82.—Shake a little paraffin oil with distilled water: an emulsion (p. 14) is formed, but this rapidly separates again into two layers. Now add a little soap solution, and shake vigorously. A more stable emulsion is formed. The **detergent action** of soap largely depends on its property of emulsifying grease in this way; the fine droplets can then be washed away with water.

Expt. 83.—Wash lampblack (fine soot) with petrol to remove grease, and dry in a steam oven. If the fine powder is shaken with water, the suspension settles on standing. But if soap solution is added, an inky suspension is formed which does not settle. The action of soap in removing dirt depends on this action.

The calcium and magnesium salts in hard water cause a larger waste of soap than corresponds with the production of the calcium and magnesium salts of the fatty acids:

$$CaCO_3 \text{ (dissd.)} + 2\ NaCO_2{\cdot}C_{17}H_{35} = Ca(CO_2{\cdot}C_{17}H_{35})_2 \text{ (ppd.)} + Na_2CO_3.$$

About 0·17 lb. of soap is required for 100 gallons of water containing 1 grain of $CaCO_3$ per gallon, instead of 0·075 lb. (theoretical). The slimy precipitate of calcium salts carries down with it some of the soap, and renders it useless. It also adheres tenaciously to the skin or fabric, and interferes with washing. The water does not acquire the smooth feeling characteristic of a **soft water** (free from dissolved calcium and magnesium salts), which is intensified by traces of alkali from the excess of soap, but retains its harsh feeling until a large excess of the soap has been added (**hard water**).

Ferrous carbonate also dissolves in water containing dissolved carbon dioxide (carbonic acid), forming ferrous bicarbonate, $Fe(HCO_3)_2$. On boiling, a reddish-brown precipitate of ferric hydroxide, $Fe(OH)_3$, is thrown down, since the ferrous carbonate is readily oxidised by the dissolved oxygen:

$$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2.$$

A similar ochre-like deposit is formed by oxidation of ferruginous water in streams. If such water is used for washing, the slimy salts formed with soap carry down brown ferric hydroxide, which adheres to the fabric in spots, forming "iron-mould." This may be removed by a hot solution of oxalic acid.

Temporarily hard waters deposit a crust or **scale** of calcium carbonate when boiled in kettles or boilers, and this interferes with the transmission of heat. It dissolves in hydrochloric acid with effervescence.

Waters containing magnesium and calcium carbonates held in solution by carbonic acid, when they fall in drops from the roofs of caves, lose the carbonic acid by evaporation and deposit the insoluble salts in the form of pendants, made up of several concentric layers, and known as **stalactites** (Fig. 112). The drops falling on the floor of the cave also deposit salts, and another concretion called a **stalagmite,** growing upwards to meet the stalactite, is formed. Small stalactites are formed under brickwork arches even in localities where the water is soft. These are derived from the calcium carbonate in the mortar, which is dissolved by the carbon dioxide in rain water.

Temporarily hard water may be **softened** by the addition of exactly the right amount of lime in the form of lime-water, or milk of lime (**Clark's process,** 1841). Calcium bicarbonate is precipitated as carbonate by adding an equivalent amount of lime :

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

But if magnesium bicarbonate is present, *double* the amount of lime must be added, when the sparingly soluble magnesium hydroxide is formed :

$$Mg(HCO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2 + 2CaCO_3 + 2H_2O.$$

Magnesium carbonate is appreciably soluble in water. One gm. dissolves per litre, as compared with 0·013 gm. per litre in the case of calcium carbonate ; the bicarbonates are about thirty times as soluble. The normal carbonate would not be precipitated, but the hydroxide is much less soluble (0·01 gm. per litre). The precipitates are allowed to settle, and the softened water is run off for use. It may be filtered through a bed of coke.

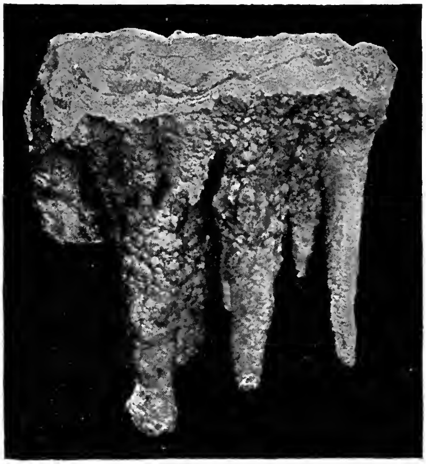


FIG. 112.—Stalactites.

A different kind of hardness is that due to the presence of the sulphates or chlorides of calcium and magnesium, derived from the soil. These are not precipitated on boiling, and cause what is called **permanent hardness.** The water may at the same time possess temporary hardness. If such waters are evaporated in boilers, gypsum ($CaSO_4,2H_2O$) is deposited as a very hard, crystalline scale, which seriously impedes the transmission of heat. This scale does not effervesce with hydrochloric acid unless carbonates are also present. Such waters cause waste of soap in laundry work for the same reason as temporarily hard water. Permanently hard waters are softened by adding a mixture of caustic soda and sodium carbonate (soda-ash, or else washing-soda, $Na_2CO_3,10H_2O$), when both temporary and permanent hardness are removed :

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4 \text{ (soluble).}$$
$$Ca(HCO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O.$$

Other materials used in laundering are: **ammonia,** $NH_4 \cdot OH$, which acts similarly to caustic soda; and **borax,** $Na_2B_4O_7,10H_2O$, which precipitates calcium borate, $CaBO_2$, and also forms a little caustic soda by hydrolysis: $Na_2B_4O_7 + 3H_2O \rightleftharpoons 2H_3BO_3 + 2NaBO_2$; $NaBO_2 + 2H_2O \rightleftharpoons NaOH + H_3BO_3$.

Hardness is not known to be injurious to water for drinking purposes (**potable water**)—in fact the presence of bicarbonates gives the water a refreshing taste, and prevents its corrosive action on lead pipes.

The **hardness** of a water is expressed in parts of calcium carbonate, $CaCO_3$, equivalent to the calcium and magnesium salts, per 100,000 parts of water, or else in grains per gallon (or parts per 70,000). It is **estimated** by finding the volume of standard soap solution which is required to produce a lather lasting five minutes with 50 c.c. of the water. The soap solution is prepared by dissolving 10 gm. of Castile soap, in fine shavings, in 250 c.c. of alcohol, on a water-bath. The solution is made up to 1000 c.c. with a mixture of 4 vols. of alcohol and 1 vol. of water. The standard hard water is prepared by dissolving 0·5 gm. of pure Iceland spar ($CaCO_3$) in hydrochloric acid, evaporating to dryness, dissolving in distilled water, re-evaporating to remove HCl, then dissolving to 1 litre in distilled water. 1 c.c. = 0·0005 gm. of $CaCO_3$. A given number of c.c. of this, made up to 50 c.c. with distilled water to give the same soap standard as the hard water, gives the hardness of the latter, in parts per 100,000. *E.g.*, if 10 c.c. of the standard hard water is required, made up to 50 c.c., to destroy the same amount of soap as 50 c.c. of the given water, the latter contains 10 parts of $CaCO_3$ per 100,000 total hardness. If 50 c.c. of the given water are boiled, filtered, and made up to 50 c.c., the residual hardness is the permanent hardness. Temporary hardness = total hardness − permanent hardness.

River water.—River water, which has previously percolated through soil, contains dissolved salts and suspended matter, both mineral (clay) and organic, from vegetable matter. Water which has flowed over peat, or peaty soil, contains dissolved organic acids (crenic and apocrenic), which give it a yellow colour, and cause it to corrode lead or iron pipes.

River water flowing over cultivated land contains, in addition to the above impurities, ammonium salts, nitrites, nitrates, sodium chloride, and organic matter of vegetable and animal origin containing nitrogen. The purity of the water depends on the nature of the soil. Thames water, flowing over soil rich in limestone, contains about 157 milligrams of calcium carbonate per litre. Trent water, flowing over soil containing gypsum, contains 300 milligrams of calcium sulphate per litre. The calcium sulphate of the Trent water at Burton is of value in brewing. The waters of the Dee and Don, draining the Aberdeen granite area, contain only traces of dissolved calcium salts.

The dissolved **oxygen** of river water is of importance to fish. One litre of river water, well aerated, contains about 50 c.c. of gas, which is composed of 20 c.c. of nitrogen, 20 c.c. of carbon dioxide, and 10 c.c. of oxygen.

Spring, or deep well, water differs from river water only in having undergone filtration through porous strata. In this way the suspended matter may be largely removed, leaving the water clear. The organic matter and nitrites may also have been more or less oxidised, but the dissolved mineral impurities usually increase. Of 100 parts of rain, only 36 flow to the sea in rivers ; the rest is either evaporated, or penetrates into the earth's crust, to reappear to some extent in springs. This type of natural water is probably the best for drinking purposes. Untreated distilled water is not suitable for drinking ; if prepared for that purpose on board ship, it must be aerated and certain salts added to make it palatable.

Sea water.—Sea water contains a large proportion of dissolved solids, about 3·6 per cent. on the average, of which 2·6 per cent. represents sodium chloride. It contains bromides, sulphates, chlorides, and carbonates of magnesium, calcium, and potassium. Traces of lithium, rubidium, cæsium, and even of gold, are present.

Mineral waters.—Natural waters containing special constituents not present (except in traces) in ordinary water are known as **mineral waters.** They are of six kinds :

(1) **Acidulous waters,** containing dissolved carbon dioxide, together with alkali bicarbonates, and common salt. The carbon dioxide may be liberated with effervescence when such waters are slightly warmed, *e.g.*, Apollinaris and Seltzer (*i.e.*, Selters) waters. Some acidulous waters contain sulphuric acid, probably derived from the oxidation of sulphur dioxide or iron pyrites.

(2) **Chalybeate,** or **ferruginous, waters,** containing ferrous carbonate held in solution by carbon dioxide as bicarbonate. On exposure to air, such water deposits a brownish-red precipitate of ferric hydroxide (p. 207). *E.g.*, Pyrmont water.

(3) **Hepatic waters** (Latin *hepar,* sulphur), containing sulphuretted hydrogen, H_2S, and alkali sulphides, *e.g.*, Na_2S. These waters smell of sulphuretted hydrogen, and on exposure to air deposit sulphur as a white, milky turbidity : $2H_2S + O_2 = 2H_2O + 2S$. Harrogate water is of this type.

(4) **Alkaline waters,** *e.g.*, Vichy water, contain sodium bicarbonate, $NaHCO_3$, and sometimes lithium bicarbonate, $LiHCO_3$, which are supposed to be beneficial in the treatment of gout.

(5) **Bitter waters** contain various dissolved salts. *E.g.*, Marienbad water (sodium sulphate) ; Epsom water (magnesium sulphate); Friedrichshall and Hunyadi-Janos waters (sodium and magnesium sulphates).

(6) **Siliceous water** contains dissolved colloidal silica (SiO_2) and alkali silicates. Such waters are those of the geysers of Iceland, New Zealand, and Yellowstone Park (America). They are usually almost boiling, and deposit masses of siliceous sinter at the mouth of the geyser.

Hot springs occur in various places, *e.g.*, Buxton (28°) and Bath (47°). They often contain dissolved gas, including helium, and traces of **radium emanation** (p. 1025), to which their medicinal properties are attributed. The presence of traces of radioactive substances may explain why artificial mineral waters, having apparently the same composition as the natural waters, do not possess the same medicinal properties as the latter.

Bacteriology of water.—Numerous types of micro-organisms may be present in natural water, mostly non-pathogenic. Germs of typhoid, cholera, or anthrax may, however, be present, and these diseases may be spread by polluted water. Sewage contamination, or excremental matter, is indicated by the presence of *Bacillus coli*, and since this is a comparatively robust organism, it may be assumed that if it has been destroyed by sterilisation the other organisms are also absent.

Water for drinking purposes is purified by **filtration** through beds of gravel, and is freely exposed to air so as to take up oxygen. It may also be **sterilised** by adding small quantities of **chlorine**, or bleaching powder, the excess of which (giving an unpleasant taste) may be removed by adding sodium sulphite. Three parts excess of available chlorine per million destroy all coliform organisms in a polluted water after half an hour's contact. The sterilisation of water by chlorine has been largely used for military purposes. Treatment with **ozone** has also been adopted as a method of sterilisation (*cf.* p. 332). A potable water should not usually contain any *Bacilli coli* in 100 c.c.

Action of water on metals.—Potable water is conveyed through iron, lead, or zinc (galvanised iron) pipes. Certain waters on passing through iron pipes lead to the growth of vegetation, which rapidly corrodes the iron, causing ferric hydroxide to be deposited. In time the pipes may be completely choked. Soft waters more than hard are likely to attack iron. Lead is rapidly attacked by distilled, or rain, water in the presence of air, forming lead hydroxide, $Pb(OH)_2$, which is appreciably soluble, or forms a colloidal solution. Hard water has much less action on lead than soft water. The action is due partly to dissolved oxygen, and partly to *free* carbonic acid.

EXPT. 84.—Two pieces of clean lead pipe are placed in two beakers containing distilled water and tap-water, respectively, the metal being only partly covered. Allow the beakers to stand for a few hours. The distilled water rapidly becomes turbid, whilst the tap-water (if hard) remains clear. Pour off the liquids, and add sulphuretted hydrogen water. Compare the brown or black colorations, due to lead sulphide. The water should not be filtered, as dissolved lead hydroxide is retained to some extent by filter-paper.

Bicarbonates in water (temporary hardness) reduce the action on lead; free carbonic acid (*e.g.*, rain water) increases the action.

Peaty waters, containing organic acids, act rapidly on lead or zinc, unless neutralised by lime.

Pure water.—There is probably no substance more difficult to obtain in a state of extreme purity than water. It is a close approach to the *alkahest*, or universal solvent, of the alchemists, since it dissolves traces of practically everything with which it is brought in contact. For chemical purposes, water is purified by **distillation.** If the intermediate portion only of the distillate is collected in good glass bottles, previously well steamed out to remove the alkaline layer from the glass, the water is very nearly pure. A copper vessel, with a pure tin or silver coil condenser, or a copper condenser without brazing, is the best apparatus to use.

Still purer water is obtained by destroying the nitrogenous organic matter, which gives off traces of ammonia on distillation, by passing chlorine through boiling distilled water for half an hour. The chlorine is boiled out, pure potash and potassium permanganate are added, and the water distilled, the first half being rejected, and a quarter only of the remainder collected. The process is repeated with this fraction. Or Nessler solution (p. 875) may be added to the water, and the latter distilled.

The dissociation of steam.—If electric sparks are passed through steam (Fig. 113), it is decomposed to a slight extent into hydrogen and oxygen: $2H_2O \rightleftharpoons 2H_2 + O_2$. The dissociation increases with the temperature. The following table gives the **percentage dissociation** at different temperatures and pressures, *i.e.*, the number of molecules decomposed out of every 100 molecules of steam.

TABLE OF DISSOCIATION OF STEAM.

$T°$ abs.	10 atm.	1 atm.	0·1 atm.	0·01 atm.
1000 … …	$1{\cdot}39 \times 10^{-5}$	$3{\cdot}00 \times 10^{-5}$	$6{\cdot}46 \times 10^{-5}$	$1{\cdot}39 \times 10^{-4}$
1500 … …	$1{\cdot}03 \times 10^{-2}$	$2{\cdot}21 \times 10^{-2}$	$4{\cdot}76 \times 10^{-2}$	0·103
2000 … …	0·273	0·588	1·26	2·70
2500 … …	1·98	3·98	8·16	16·6

Thus, at the melting point of platinum (1755°) and 760 mm. pressure, about 6 molecules of steam in every thousand are dissociated into detonating gas. At 7·6 mm. pressure this number has increased to 27.

The dissociation of steam was discovered by Grove (1847), who heated a platinum wire electrically in steam, passed sparks through steam, and plunged the fused end of a platinum wire into water. In 1863, Deville poured more than a kilogram of fused platinum into water, and found that detonating gas was freely evolved. By passing a stream of moist carbon dioxide through a porcelain tube heated to 1300°, and absorbing the gas in potash, he obtained 25 c.c. of detonating gas in two hours.

The combining volumes of hydrogen and oxygen.—The composition of water by weight has already been dealt with (p. 60), and the approximate composition by volume also was considered. Early experiments on this ratio are those of Cavendish (1781), who obtained the ratio H/O by volume 201 : 100; Gay-Lussac and Humboldt (1805), who found 199·89 : 100; and Bunsen, whose numerous determinations indicated an almost exact ratio of 2 : 1.

The accurate determination of the combining volumes was attempted by Alexander Scott, whose experiments, made in 1887–9 and 1893, at first yielded slightly varying ratios, from 199·4 : 100 to 200 : 100. The later experiments showed that this variation was due to a very thin film of grease carried over from the lubrication of the stopcocks into the eudiometer, which took up a little oxygen during the explosion, burning to carbon dioxide and steam. By using pure hydrogen, prepared by passing steam over sodium, and pure oxygen from silver oxide (p. 159), and by lubricating the stopcocks with syrupy phosphoric acid, the combining ratio, at S.T.P., was found to be a little greater than 2 : 1, viz., 200·285 : 100.

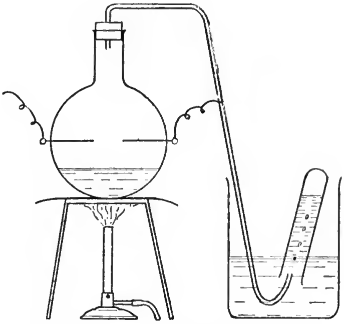


FIG. 113.—Dissociation of Steam by Electric Sparks.

Morley, by burning the gases in his apparatus, and measuring the residual gas, found 200·269 : 100.

The most recent determination of the ratio is that of P. F. Burt and E. C. Edgar, made at Owens College, Manchester (1915). A short description of this research is given here as an illustration of the refinements now possible in work carried out with gases. The final result was 200·288 : 100, agreeing with Scott's to within 3 parts in 200,000.

The special points of this research were: (1) very carefully purified gases were used; (2) the actual measurements were carried out at 0°, and under 1 atm. pressure, so that the temperature and pressure corrections were eliminated. The **hydrogen** was prepared by the electrolysis of recrystallised barium hydroxide (p. 186); it was dried by phosphorus pentoxide, and further purified in two ways: (i) by passing over charcoal cooled in liquid air, which readily absorbs oxygen and nitrogen, but hydrogen only to a slight extent; (ii) by passing through a tube of palladium black to remove oxygen as water, and then pumping the gas through the walls of a closed palladium tube heated electrically. The palladium tube was welded to a short platinum tube, and the latter sealed into a glass tube. This was sealed inside a wider tube, and the palladium heated by a platinum spiral wound on a quartz cylinder slipped over it. The palladium was protected from mercury vapour from the pumps by plugs of gold wire sponge. The palladium was charged with hydrogen at 100°, 300 c.c. of gas were then pumped off at 180°, and the metal was recharged with hydrogen at 100°. The **oxygen** was prepared: (1) by the electrolysis of baryta, liquefaction in fresh liquid air, and fractionation; (2) by heating pure potassium permanganate in glass tubes, and washing the gas (*a*) with strong caustic potash solution, (*b*) with saturated baryta solution, (*c*) with very strong potash solution. The gas was then dried by sticks of potash, and phosphorus pentoxide, liquefied, and fractionated.

The apparatus (Fig. 114) consisted of a glass 300 c.c. pipette, *A*, sealed to capillary tubes at each end. The lower capillary was expanded to a dead-space, *B*, of about 1 c.c. capacity, with a glass levelling-point. The upper capillary led to a 3-way tap, *C*. The pressure of the gas in the bulb was equal to the vertical distance between the mercury surface in *B* and in the upper chamber, *D*, also provided with a levelling-point, and these two vessels were kept at a constant distance apart by a stout glass rod sealed between them. The manometer head passed to a mercury pump. The T-piece, *H*, and the tap, *J*, formed a *volume adjuster*; the capacity of the pipette could be varied within narrow limits by withdrawing mercury from *J*; this mercury could be weighed, and its volume thus accurately determined. The bulb and upper part of the apparatus were enclosed in an ice-bath; the lower dead-space was surrounded by a small brine bath, *M*. The mercury for displacing the gas was contained in *O*; the air-catch, *P*, protected the pipette from air leaks through the rubber. The volume of the apparatus, from *C* to the level of the glass point in the dead-space, *D*, was determined by weighing the contained mercury. The exit tubes from the oxygen and hydrogen apparatus joined beyond the taps, *X* and *Y*, in a T-piece, *Q*, which divided again, one branch leading to the pump through *R* and the other to the measuring pipette, *A*. The gas was allowed to enter the pipette, displacing mercury into *O*, until the mercury surfaces in the dead-space and manometer stood at the glass points. Since there was a vacuum above the mercury in the manometer, the gas was measured under the pressure of this mercury column, which was very approximately 1 atm. The tap *X*, or *Y*, was then closed, and the fine adjustment made by the pressure adjuster, J, by which small amounts of gas could be added to, or removed from, the pipette.

The gas had previously been allowed to attain the temperature of the ice-bath, which took about three hours, and was then passed to the explosion bulb, Z, by opening C and raising O, mercury being displaced from Z through an air-trap, α, to the reservoir, β. Z had a capacity of about 1 litre. Two pipettes of hydrogen with a little excess, measured by the pressure adjuster, were thus passed into Z. A pipette of oxygen was then added in portions, firing after each addition. The small residual volume of wet hydrogen was sparked for a few minutes. The explosion vessel was then cooled by a mixture of solid carbon dioxide and acetone to

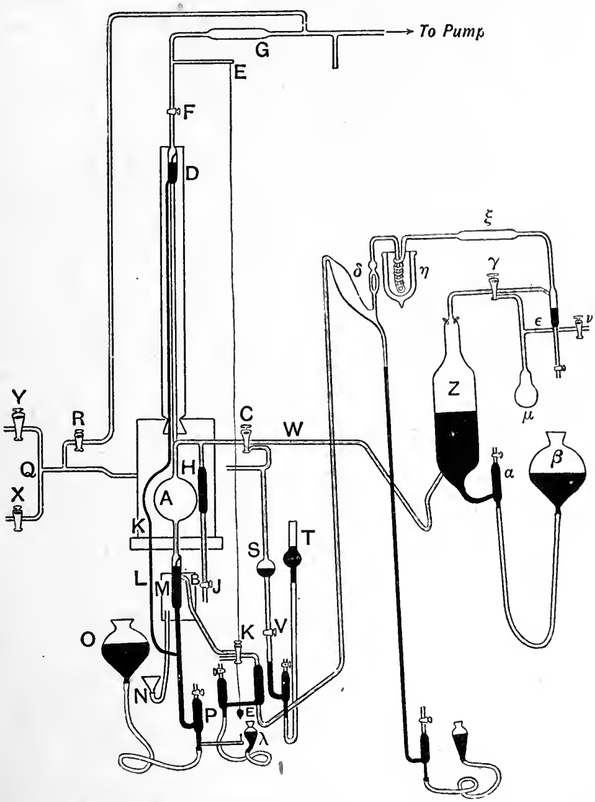


FIG. 114.—Volumetric Composition of Water: Apparatus of Burt and Edgar.

freeze the water, the pressure reduced, and the residual gas sucked off through a phosphorus pentoxide tube into a small pump, δ, a spiral, η, cooled in liquid air, being also interposed. The gas collected in the small vessel, E, and its volume was measured as follows. The pipette, A, was filled with hydrogen from the generator, and carefully levelled. The small volume of residual gas was then added from E, and the pressure adjustment made by running a little mercury from the adjuster. From the weight of this mercury the volume of the residual gas was calculated.

The results of 59 experiments gave the ratio **2·00288 vols. of hydrogen : 1 vol. of oxygen at S.T.P.**

From the results of these experiments on the volumetric composition of water, we can calculate the ratio of the hydrogen and oxygen *by weight* from a knowledge of the *densities* of the gases. The weights of 1 litre of hydrogen and oxygen at S.T.P. are, according to Morley (p. 72), 0·089873 gm. and 1·42900 gm., respectively. There is some evidence that Morley's value for oxygen is a little too low, by about 1 part in 28,000. Thus, Germann (1914), using carefully fractionated liquid oxygen, found 1·42906, and the same number was found by Scheurer in 1913. Rayleigh had previously found 1·42904. Morley's value for hydrogen is probably the most exact we possess. Adopting Morley's figures, the values of Burt and Edgar give, for **the weight of oxygen combining with 1 part by weight of hydrogen**:

$$\frac{1{\cdot}42900}{2{\cdot}00288 \times 0{\cdot}089873} = \mathbf{7{\cdot}938}.$$

The composition of water.—The following table gives some of the results of accurate investigations on the composition of water by weight and volume, and the ratio of the densities of hydrogen and oxygen.

Experimenters.	**Ratio of densities O/H** (at S.T.P.)	**Ratio of combining volumes H/O** (at S.T.P.)	**Atomic weight of oxygen** (H = 1)
Dumas and Boussingault (1841)	15·9015	—	—
Regnault (1845)—corrected ...	15·91	—	—
Rayleigh (1882)	15·884	—	—
Cooke and Richards (1888) ...	—	—	15·869
Rayleigh (1889)	—	—	15·890
Cooke (1889)	15·890	—	—
Noyes (1890)	—	—	15·897
do.. (1907)	—	—	15·8799
Morley (1895)	15·9002	2·00269 : 1	15·8792
Scott (1893)	—	2·00285 : 1	—
Thomsen (1895–6)	15·8878	—	15·869
Keiser (1898)	—	—	15·8799
Burt and Edgar (1916)	—	2·00288 : 1	—

These results offer an excellent example of the **quantitative method** in chemical investigation. Starting from the *assumption* that the composition of water is invariable, within the narrowest limits of experimental error, the different experimenters set out to determine this composition. The close agreement of the results confirms the original assumption, which is a special case of a law of very great importance (p. 110).

EXERCISES ON CHAPTER XII

1. Describe briefly the important physical properties of water in its different states. How would you identify a specimen of water ?

2. Classify the various forms of natural waters. How may pure water be prepared from these ?

3. What is meant by the hardness of water ? To what is it due, and how may it be removed ? One hundred c.c. of water required 4·5 c.c. $n/50 H_2SO_4$ for neutralisation with methyl-orange. What weight of quicklime must be added, in the form of lime-water, to soften 100 gallons of this water ?

4. What varieties of mineral waters occur ? How would you test a specimen of mineral water to decide its character ?

5. What is the action of (*a*) distilled water, (*b*) hard water, on lead ? How would you attempt to reduce the plumbosolvent action of water ?

6. Describe an experiment to illustrate the dissociation of steam at high temperatures. What precautions are necessary to prevent recombination on cooling ?

7. What are the exact combining volumes of hydrogen and oxygen ? How have they been determined ?

8. The formula of water was formerly written HO. What is the atomic weight of oxygen corresponding with this formula, and why is the formula H_2O now used ? What is the formula of liquid water ?

CHAPTER XIII

COMMON SALT. HYDROCHLORIC ACID. CHLORINE

Common salt.—After air and water, there is probably no material so familiar as **common salt,** which is mentioned in the oldest historical records we possess. It is an essential constituent of food, about 29 lb. per head of population being annually consumed in this way. About 13,000,000 tons of salt were produced in 1896; in 1907 there were nearly 2,000,000 tons made in Great Britain alone. Common salt occurs abundantly, and is very widely distributed in nature. It is contained in small quantities in all the **primary rocks.** From these it has passed by the action of water to **rivers,** and thence to the **sea,** where the water re-evaporates whilst the salt remains. Average sea-water contains about 3 per cent. of salt. The extensive **deposits of rock-salt,** found in the earth in many localities, appear to have been produced by the evaporation of former seas and lakes.

FIG. 115.—Rock Salt Crystals.

Rock-salt, or **halite,** is the crystalline variety, occurring in all the continents either as cubic crystals (Fig. 115), which are colourless when pure but are often tinged yellow, brown, or sometimes blue, by impurities, or else in large more or less coloured masses, which have a cubic cleavage. Very extensive deposits occur at Wieliczka (Poland), Cardona (Spain), in Austria, Germany, and in England. The richest English deposits are in the Cheshire district, at Northwich and Winsford, in the upper Trias formation. The top bed at Northwich is 135–150 ft. below the surface, and is 75 ft. thick. It is followed by a second bed 105 ft. thick, separated from the first by 30 ft. of hard marl. Thinner beds occur below.

Besides rock-salt, there are **brine springs,** yielding a nearly saturated solution of salt. A saturated solution contains 35·78 parts of salt per 100 of water at 15°, or about 26 per cent. The solubility increases only very slowly with rise of temperature (p. 99). From this brine, salt was prepared by the Romans during their occupation of Britain, by evaporation in square lead pans holding a few gallons. With the difference that flat iron pans holding several thousand gallons of brine are now used, the modern process of salt manufacture in Cheshire is the same as that of the Romans.

The brine is tapped by bore-holes sunk through the marl; if no brine is found, water is poured down, becomes nearly saturated with salt, and is pumped directly to the evaporating pans. Large cavities are formed by the dissolving out of the salt deposits, and serious subsidences of land often occur.

An analysis of Northwich **brine** is as follows:—

Sodium chloride (common salt)	25·790	per cent.
Calcium sulphate	0·450	,, ,,
Magnesium chloride	0·093	,, ,,
Calcium carbonate	0·018	,, ,,
Calcium chloride	0·044	,, ,,
Water	73·605	,, ,,

The more slowly the evaporation proceeds, the larger are the crystals deposited in the pans. The different grades, according to fineness, are: **fine, or table, salt; manufacturer's salt; fishery salt,** and **bay salt** (usually in the form of floating "hoppers," or cubes with hollow faces, Fig. 116). In some works the brine is evaporated in **vacuum pans** under reduced pressure. These are iron boilers heated by steam coils (Fig. 117), the steam produced by evaporation in one pan passing to the coils of the next. The steam from the last pan, which is under low pressure, is condensed by injecting cold water into it at *P*, and removing the extricated air along with the water by a pump to preserve the vacuum. Each pan has a long leg dipping into an open trough, into which the salt falls. The length of this liquid column balances the vacuum in the pan, and thus acts as a brine barometer.

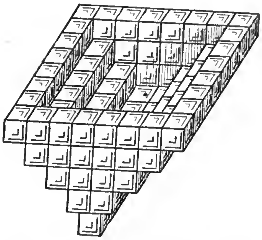


FIG. 116.—"Hopper Crystals" of Common Salt.

In warm climates (*e.g.*, in the South of France) sea-water is evaporated in large flat ponds, called **salt meadows,** by the heat of the sun; the salt so made is called **solar salt.** The mother-liquor, called **bittern,** contains the magnesium salts and bromides (p. 393) of the sea-water. This process was formerly carried on, previous to boiling, at Hayling Island, near Portsmouth, and at Lymington.

The industrial uses of common salt.—Besides its use in flavouring food and assisting digestion, common salt finds a large number of applications in industry. It is used in melting snow and ice on roads, an effect due to the lowering of the freezing point of water by the dissolved salt (p. 103). Salt is used in glazing common earthenware, such as drain pipes; salt is thrown into the furnace in which the goods are fired, and is volatilised. The vapour forms a fusible silicate (glaze) with the silica of the clay, and hydrochloric acid is evolved: $SiO_2 + 2NaCl + H_2O = Na_2SiO_3 + 2HCl$. Unsuccessful attempts have been made to produce sodium carbonate and hydrochloric acid in this way on a large scale. Very large quantities of salt are used in the **alkali industry,** for producing sodium carbonate and caustic soda, and salt is also largely used in preserving fish and other foods.

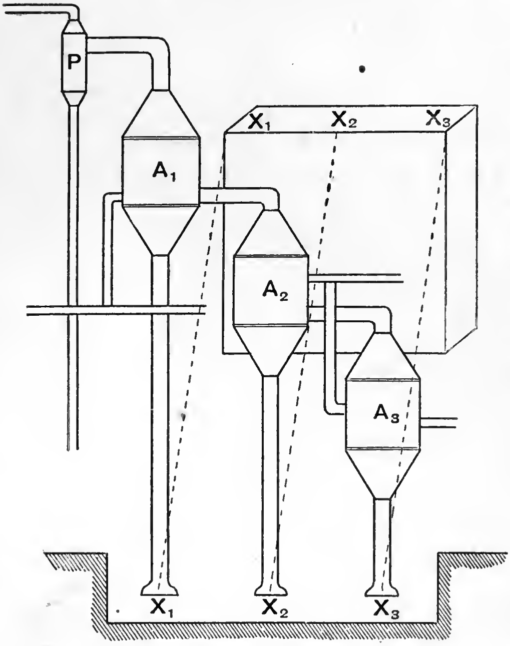


FIG. 117.—Vacuum Evaporation Pans.

The history of chlorine.—By distilling common salt with concentrated sulphuric acid, Glauber (1648) obtained white fumes which could be condensed in water in a receiver, forming an acid liquid, called **spirit of salt.** The residue in the retort when dissolved in water, deposited large transparent crystals known as **Glauber's salt.** In 1772 Priestley found that the product of the action of sulphuric acid on salt was a permanent gas, which could be collected over mercury, but was very soluble in water. The solution of the gas was spirit of salt, which was then called the **marine**

acid, or **muriatic acid** (from Latin *muria* = brine). Lavoisier (1789), in speaking of the acid, was able to say only that: "we have no idea whatever of the nature of its radical, and only conclude, from analogy with the other acids, that it contains oxygen as its acidifying principle." Muriatic acid was, therefore, regarded as the oxide of an unknown element.

In 1774 Scheele examined the action of muriatic acid on black oxide of manganese, or manganese dioxide. He found that this dissolved in the cold acid with the production of a dark brown solution, which on warming gave off a greenish-yellow gas, which had a powerful odour of *aqua regia,* and bleached vegetable colours. Scheele regarded this gas as muriatic acid deprived of its phlogiston by the manganese, and since he considered hydrogen to be phlogiston (p. 41), this amounts to the same thing as muriatic acid deprived of hydrogen: **Muriatic acid—H.** This is correct.

In 1785 Berthollet found that when a solution of the new gas in water was exposed to light, it gave off bubbles of oxygen and left a solution of muriatic acid. In accordance with Lavoisier's theory of acids, he therefore considered that the gas was a compound of muriatic acid and oxygen, or **oxymuriatic acid.** He recognised, however, that it was not an acid, which was a serious difficulty from the point of view of this theory.

Gay-Lussac and Thenard in 1809 heated sodium in muriatic acid gas, and found that hydrogen was evolved and common salt remained. The hydrogen, they supposed, came from water existing in combination in the gas, but they were unable to obtain oxygen from the latter or to oxidise charcoal heated to whiteness in the gas. Nevertheless, they decided in favour of Lavoisier's view, and rejected the alternative that the gas was a compound of "oxymuriatic acid," which was really an element, and hydrogen.

The elementary nature of oxymuriatic acid was, however, strongly urged by Davy in 1810. He heated charcoal, sulphur, and metals in the gas, but never obtained any known oxygen compound. He proposed to regard it as an element, and called it **chlorine** (Greek *chloros* = pale green). In Berthollet's experiment, the oxygen came from the water, the hydrogen of which united with the chlorine to form muriatic, or hydrochloric, acid: $H_2O + Cl_2 = 2HCl + O$. Dry chlorine, Davy found, did not bleach. "I merely state what I have seen," says Davy, "and what I have found. There *may* be oxygen in oxymuriatic gas, but I can find none." After a little controversy, this view was accepted.

The preparation of chlorine.—Chlorine is prepared in the laboratory by **the oxidation of hydrochloric acid**: $2HCl + O = H_2O + Cl_2$. The operation may be carried out in several ways, according to the oxidising agent employed. Atmospheric oxygen, in the presence of a copper salt acting as a catalyst, may be used; or substances rich in oxygen which readily part with that element, such as manganese dioxide, MnO_2; potassium permanganate, $KMnO_4$; potassium dichromate, $K_2Cr_2O_7$; and bleaching powder, $CaOCl_2$:—

$4HCl + O_2 = 2H_2O + 2Cl_2$ (atmospheric oxygen);

$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$ (manganese dioxide);

$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$ (potassium permanganate);

$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$ (potassium dichromate);

$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2$ (bleaching powder).

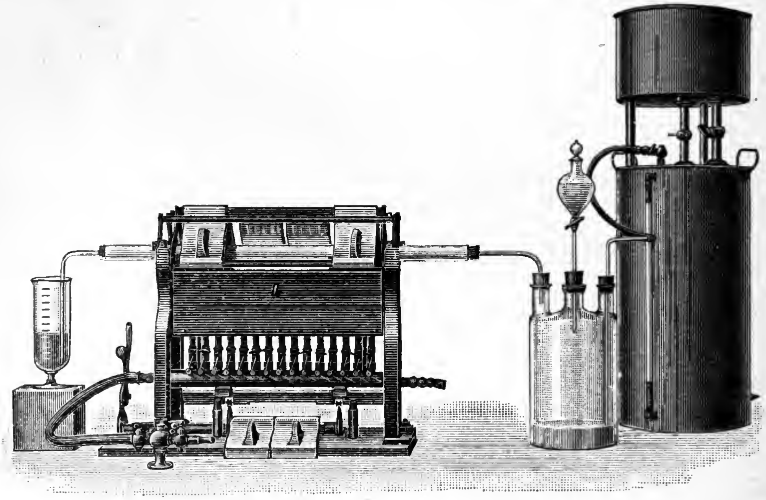


FIG. 118.—Oxidation of Hydrochloric Acid Gas by Atmospheric Oxygen with formation of Chlorine.

EXPT. 85.—A stream of air is passed through concentrated hydrochloric acid in a Woulfe's bottle, and concentrated sulphuric acid allowed to drop slowly into the latter. The mixture of air and hydrochloric acid gas is passed through a hard glass tube packed with pieces of pumice which have been soaked in a solution of copper sulphate and dried, and the tube is heated in a furnace (Fig. 118) to a dull red heat. The gas is then passed through litmus solution, which is rapidly bleached by the chlorine evolved.

EXPT. 86.—Place powdered manganese dioxide in one bulb of a hard glass tube, leaving the other bulb empty. Pass a current of hydrochloric acid gas, obtained by dropping concentrated hydrochloric acid into concentrated sulphuric acid in the apparatus of Fig. 81, over the dioxide, and allow the gas to pass into a bottle containing litmus solution and a piece of moist red flannel (Fig. 119). The litmus is turned red. Now heat the manganese dioxide. Moisture collects in the second bulb, and the bottle becomes filled with a greenish-yellow gas, which bleaches the litmus and the red flannel. This is **chlorine.**

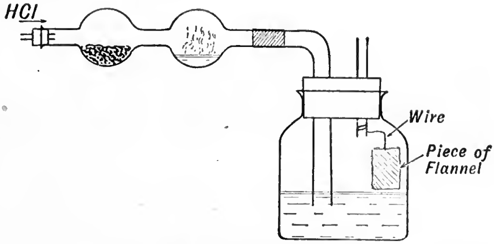


FIG. 119.—Oxidation of Hydrochloric Acid Gas by heated Manganese Dioxide.

The usual method of preparing chlorine is to decompose hydrochloric acid with manganese dioxide: the mineral form, called *pyrolusite,* in small pieces, is most convenient.

EXPT. 87.—One-third fill a litre flask with small pieces of pyrolusite, and fit the flask with a good black rubber stopper, carrying a dropping funnel and delivery tube connected with a wash-bottle containing a little water, to remove hydrochloric acid gas, and a second bottle containing concentrated sulphuric acid (Fig. 120). Pour 200 c.c. of concentrated hydrochloric acid into the flask. Notice the formation of a dark brown solution. Heat gently on wire-gauze, or in a water-bath, and collect the chlorine in jars by downward displacement (it is $2\frac{1}{2}$ times as heavy as air). The preparation is carried out in a good draught cupboard, as the gas has a powerful corrosive action

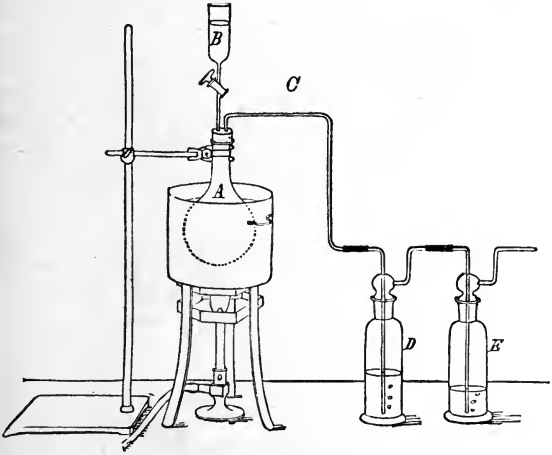


FIG. 120.—Preparation of Chlorine from Aqueous Hydrochloric Acid and Manganese Dioxide.

on the mucous membrane. The inhalation of alcohol vapour, and diluted ammonia gas, relieves the bad effects produced by breathing chlorine.

The action of manganese dioxide on hydrochloric acid proceeds in two stages. The dark brown solution formed in the cold contains a higher chloride of manganese, $MnCl_4$ or $MnCl_3$, which breaks up on warming, with liberation of chlorine :

(1) $MnO_2 + 4HCl = MnCl_4 + 2H_2O$. (2) $MnCl_4 = MnCl_2 + Cl_2$; or (1*a*) $2MnO_2 + 8HCl = 2MnCl_3 + Cl_2 + 4H_2O$. (2*a*) $2MnCl_3 = 2MnCl_2 + Cl_2$.

If the dark brown solution is poured into water, hydrated manganese dioxide is precipitated : $MnCl_4 + 2H_2O = MnO_2 + 4HCl$.

A mixture of 5 parts of powdered MnO_2, 11 parts of common salt, and 14 parts of 50 per cent. H_2SO_4 may also be heated in a flask to produce chlorine ; this was the method used by Berthollet (1785), but is less convenient than that of Scheele : $4\,NaCl + MnO_2 + 3H_2SO_4 = Cl_2 + 2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O$.

Expt. 88.—If red crystals of potassium dichromate are heated in a flask with concentrated hydrochloric acid, a green solution of chromic chloride, $CrCl_3$, is formed, and practically pure chlorine is evolved.

Expt. 89.—The most convenient method of preparing small quantities of chlorine is to drop concentrated hydrochloric acid slowly on crystals of potassium permanganate in a flask (Fig. 81). The gas is evolved in the cold, and may be washed with water and concentrated sulphuric acid. When the evolution of gas ceases, a further supply is obtained on warming the dark brown solution formed ; this becomes nearly colourless.

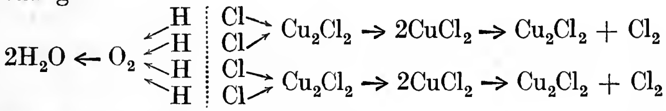
Expt. 90.—If concentrated hydrochloric acid is dropped on bleaching powder in the above apparatus, chlorine is evolved. The bleaching powder may first be mixed with one-fourth its weight of plaster of Paris, moistened slightly, pressed and cut into cubes, which are dried at the ordinary temperature. These evolve chlorine if treated in a Kipp's apparatus with concentrated hydrochloric acid, and the evolution of gas may be controlled in the usual way (p. 185).

Pure chlorine may be obtained by heating **platinic chloride,** $PtCl_4$, or **auric chloride,** $AuCl_3$ (gold chloride), in a hard glass tube. Lower chlorides are first produced, which decompose, giving the metals, at higher temperatures :

$$PtCl_4\ (\textbf{platinic chloride}) \overset{300^\circ}{=} PtCl_2\ (\textbf{platinous chloride}) + Cl_2 \overset{500^\circ}{=} Pt + 2Cl_2.$$

$$2AuCl_3\ (\textbf{auric chloride}) \overset{175^\circ}{=} 2AuCl\ (\textbf{aurous chloride}) + 2Cl_2 \overset{185^\circ}{=} 2Au + 3Cl_2.$$

Cupric chloride, $CuCl_2$, when heated to about 350°, decomposes into **cuprous chloride,** $CuCl$, and chlorine: $2CuCl_2 = 2CuCl + Cl_2$. The cuprous chloride is stable at high temperatures and does not further decompose. The **catalytic action** of cupric chloride in the oxidation of hydrogen chloride by atmospheric oxygen (p. 222), or pure oxygen gas, has been explained as follows. The cupric chloride first decomposes, with evolution of chlorine, and leaves cuprous chloride: $2CuCl_2 = Cu_2Cl_2 + Cl_2$. By the action of hydrogen chloride and oxygen on the cuprous chloride, cupric chloride and water are formed: $2Cu_2Cl_2 + 4HCl + O_2 = 4CuCl_2 + 2H_2O$. The cupric chloride again decomposes, and thus undergoes a cycle of chemical changes (*cf.* p. 167). It may be assumed, following Mercer, that the attraction of cuprous chloride for chlorine, with the attraction of oxygen for hydrogen, can together decompose the hydrogen chloride, but each acting separately is unable to effect any change:



Silver chloride, $AgCl$, on heating does not decompose, but melts at 460° to a dark yellow liquid. This conducts an electric current, and if the electrolysis is carried on in a Jena glass U-tube with gas-carbon poles, pure chlorine is evolved at the positive pole and silver deposited at the negative.

The properties of chlorine.—Chlorine is a **greenish-yellow gas,** the normal density of which is 3·220 gm. per litre. The relative density at S.T.P. is therefore 35·80. The relative density calculated from the atomic weight is 35·2, and the somewhat higher observed density may indicate a slight polymerisation: $2Cl_2 \rightleftharpoons Cl_4$. The density decreases slightly with rise of temperature, and becomes normal at about 240°, remaining at this value up to 1200°:

Temperature°	0	40	80	120	160	200	240	1200
Relative density ..	35·8	35·7	35·6	35·5	35·4	35·3	35·2	35·2.

The density at 1150° was found by Reinganum (1905) by comparing the volumes of gas displaced from a small quartz Victor Meyer apparatus, in one case filled with oxygen and in the other with chlorine. They were equal, hence no dissociation had occurred. Meier and Crafts (1881) obtained the same result by displacing oxygen by chlorine, or chlorine by oxygen, in a porcelain apparatus at 1350°. Victor Meyer and Langer (1885), by burning gas-carbon in a powerful blast of oxygen, claimed to have attained a temperature of 1700°, at which the density of chlorine fell to 29·03, which would correspond with a 35 per cent. dissociation into atoms: $Cl_2 \rightleftharpoons 2Cl$. Pier (1908) found a dissociation of Cl_2 above 1450°.

Chlorine, when cooled in solid carbon dioxide and ether, condenses to an **orange-yellow liquid,** boiling at – 33·6°. On cooling in liquid air, this forms a **pale yellow solid,** melting at – 102°. The critical temperature of chlorine is 146°; its critical pressure is 93·5 atm. The gas is liquefied at 0° by a pressure of 3·66 atm.; at 20°, 6·62 atm. pressure is required.

The chemical properties of chlorine.—The chemical properties of chlorine may be summed up in the statement that it is **a very active element;** it combines readily with hydrogen, and directly with most metals, and non-metallic elements except nitrogen, oxygen, and carbon. Combination often occurs when the elements are brought together at the ordinary temperature, often with the production of flame, or incandescence.

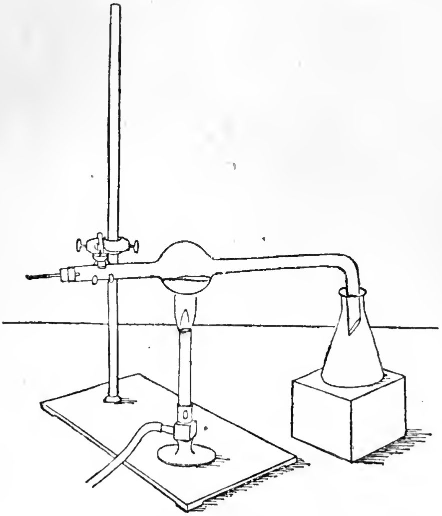


FIG. 121.—Combustion of Sodium in Chlorine.

The reaction with metals, which occurs violently with moist gas, does not take place if the chlorine is **dry,** except in the case of mercury, which completely absorbs pure dry chlorine. Sodium may be distilled in dry chlorine without reaction taking place (Wanklyn, 1883). The reason for the action of moisture is not known. In the following experiments, therefore, unless otherwise directed, **moist chlorine** is to be used.

EXPT. 91.—Sprinkle a little finely powdered **arsenic,** and **antimony,** into jars of chlorine. The substances burn brilliantly, producing **poisonous** fumes of the chlorides $AsCl_3$, $SbCl_3$, and $SbCl_5$.

EXPT. 92.—A piece of **phosphorus** in a deflagrating spoon ignites spontaneously in chlorine, burning with a pale flame, and producing fumes of the chlorides PCl_3 and PCl_5.

EXPT. 93.—Pass chlorine over a piece of **sodium** heated in a hard glass bulb tube (Fig. 121). When strongly heated, the metal catches fire and burns with an exceedingly brilliant yellow flame, producing white sodium chloride, NaCl.

Expt. 94.—A carefully dried bolt-head flask fitted with a rubber stopper and stopcock is loosely filled with leaves of **Dutch metal** (an alloy of composition copper 80 + zinc 20). The flask is then evacuated and filled with **dry** chlorine from a bell-jar standing over concentrated sulphuric acid (Fig. 122). No action occurs. The stopper is removed and a drop of water is allowed to fall into the flask: the metal at once catches fire and burns, producing yellow fumes ($CuCl_2$ and $ZnCl_2$). A spiral of German-silver wire, tipped with Dutch metal, ignites and burns when introduced into a jar of moist chlorine, throwing off a shower of sparks.

Expt. 95.—A jet of hydrogen burning in air continues to burn, with an enlarged greenish flame, when introduced into a jar of chlorine (Fig. 123), producing fumes of hydrochloric acid: $H_2 + Cl_2 = 2HCl$. These redden moist litmus paper. A jet of chlorine burns when introduced into an inverted jar of hydrogen which is burning at the mouth.

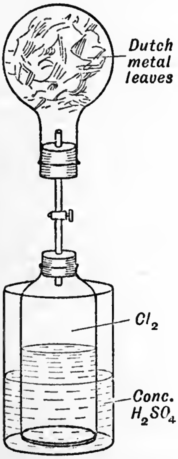


Fig. 122.—Filling a flask containing Dutch Metal with Dry Chlorine.

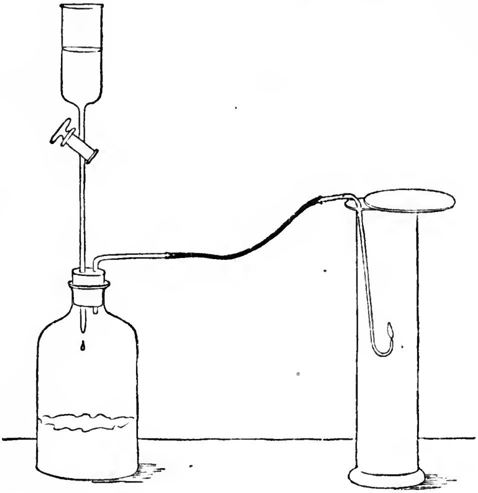


Fig. 123.—Combustion of Hydrogen in Chlorine.

Expt. 96.—A piece of dry red flannel, and some dry litmus paper, suspended in a jar of chlorine, into which some concentrated sulphuric acid has been poured, are not bleached. If a little steam is passed in, bleaching at once occurs (*cf.* p. 223).

Expt. 97.—A burning taper plunged into a jar of chlorine burns with a small dull-red flame, clouds of black carbon and white fumes of hydrochloric acid being evolved. Wax is a mixture of **hydrocarbons,**

C_nH_{2n+2}; the chlorine removes the hydrogen, forming HCl, and sets free the carbon, with which it does not combine directly. Charcoal heated to redness in a deflagrating spoon ceases to burn in chlorine.

Expt. 98.—A mixture of 2 vols. of chlorine and 1 vol. of **ethylene** (p. 675), C_2H_4, when ignited, burns with a red flame, emitting dense black clouds of carbon: $C_2H_4 + 2Cl_2 = 2C + 4HCl$.

Expt. 99.—A mixture of 2 vols. of chlorine and 1 vol. of **methane** (p. 672), CH_4, prepared out of direct sunlight, ignited with a taper, burns with a feeble whistling noise, giving fumes of hydrochloric acid and a cloud of carbon: $CH_4 + 2Cl_2 = C + 4HCl$.

Expt. 100.—A little **turpentine,** $C_{10}H_{16}$, warmed in a test-tube and poured on filter-paper, catches fire when plunged into chlorine, giving a black cloud of carbon and fumes of hydrochloric acid.

Chlorine **combines** with the gases **sulphur dioxide,** SO_2, **carbon monoxide,** CO, and **ethylene,** C_2H_4, producing **sulphuryl chloride,** SO_2Cl_2, **carbonyl chloride** (phosgene), $COCl_2$, and **ethylene dichloride,** $C_2H_4Cl_2$, respectively. The carbon monoxide and sulphur dioxide react with chlorine in presence of animal charcoal; ethylene combines directly with chlorine if the mixture of gases is exposed to light, an oily liquid being formed.

Chlorine water.—Chlorine is fairly soluble in water, 2 volumes of the gas dissolving in 1 volume of water at 15°. The solution, which may be prepared by passing chlorine through cold water in Woulfe's bottles, is pale yellow in colour, and smells strongly of the gas. It is called **chlorine water.** The solution possesses bleaching and oxidising properties. It precipitates sulphur from a solution of sulphuretted hydrogen: $H_2S + Cl_2 = 2HCl + S$; it liberates iodine from a solution of potassium iodide: $2KI + Cl_2 = 2KCl + I_2$, but with an excess of chlorine water the iodine dissolves, forming iodine chloride, ICl. A solution of sulphur dioxide (sulphurous acid) is oxidised to sulphuric acid: $2H_2O + Cl_2 + SO_2 = H_2SO_4 + 2HCl$.

When a flask of chlorine water, inverted in a basin of the same liquid, is exposed to bright sunlight, it is decomposed with evolution of bubbles of oxygen, and a solution of hydrochloric acid is left: $2H_2O + 2Cl_2 = 4HCl + O_2$.

Chlorine hydrate.—If chlorine is passed into water cooled in ice, greenish-yellow crystals separate. This substance, discovered by Berthollet in 1785, is **chlorine hydrate:** its composition has been variously stated to be $Cl_2,10H_2O$ (Faraday, 1823), $Cl_2,8H_2O$ (Roozeboom, 1884), and $Cl_2,7H_2O$ (de Forcrand, 1902). When gently warmed, the crystals melt with effervescence, and chlorine is evolved. If the experiment is performed in the dark, the gas, after drying, is perfectly pure (Harker, 1892).

EXPT. 101.—If crystals of chlorine hydrate are sealed up in one limb of a strong bent tube, and the other limb is cooled in ice and salt (Fig. 124), **liquid chlorine** distils into the cooled part of the tube when the other is warmed to about 30°.

Hydrogen chloride, or hydrochloric acid, HCl.—Chlorine and hydrogen form only one compound, **hydrogen chloride,** or **hydrochloric acid,** HCl. This is formed by the combustion of hydrogen in chlorine, but is usually prepared by the action of slightly diluted sulphuric acid on common salt: $NaCl + H_2SO_4 = NaHSO_4 + HCl$. One only of the two hydrogen atoms of sulphuric acid is expelled, and the **acid salt,** $NaHSO_4$, **sodium hydrogen sulphate,** or **sodium bisulphate** ($Na_2O,2SO_3,H_2O$) is formed unless the temperature is higher than can conveniently be attained in a glass flask. This salt, which contains one of the hydrogen atoms of the sulphuric acid, has a strongly acid reaction in solution, and neutralises caustic soda, or sodium carbonate, with formation of the **normal salt,** Na_2SO_4. This crystallises from water as $Na_2SO_4,10H_2O$, which is **Glauber's salt.** If the acid salt is strongly heated with common salt, the remaining hydrogen atom is displaced as hydrochloric acid, and the normal salt formed: $NaHSO_4 + NaCl = Na_2SO_4 + HCl$. The hydrogen of sulphuric acid can be displaced in two stages, with formation of acid salts and normal salts, hence sulphuric acid is called a **dibasic acid.** Hydrochloric acid, which contains only one atom of hydrogen, forms only one series of salts, the normal salts, and is called a **monobasic acid.**

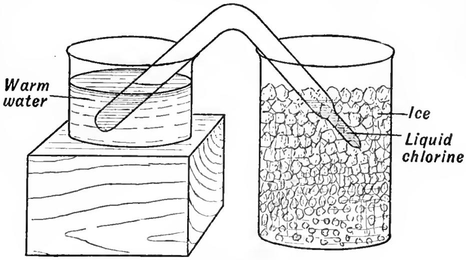


FIG. 124.—Liquefaction of Chlorine.

EXPT. 102.—The preparation of the gaseous acid is carried out in the apparatus shown in Fig. 125. Common salt is placed in the flask, and covered with diluted sulphuric acid, prepared by adding 11 vols. of concentrated sulphuric acid to 8 vols. of water, and cooling. When the flask is gently heated on wire gauze, a steady stream of hydrochloric acid gas is evolved. This is passed through a small wash-bottle containing concentrated sulphuric acid, and then collected in dry jars by downward displacement, since it is 1·27 times as heavy as air, and is very soluble in water. It may also be collected over mercury. When the jar is full of gas, dense white fumes issue from the mouth. These are formed from the gas and atmospheric moisture, producing minute droplets of solution, which have a lower vapour pressure than the partial pressure of water vapour in the air. The dry gas is quite transparent.

If the gas is passed into a flask of distilled water, kept cool by running water over the outside from a ring of perforated lead pipe placed over the neck (Fig. 126), an aqueous solution of the acid—spirit of salt—is produced. Each bubble of gas at once condenses as it leaves the delivery tube, and a considerable amount of heat is given out. The concentrated solution fumes strongly in the air.

Hydrogen chloride is very soluble in water. When 1 kgm. of water is saturated with the gas at 15° it increases in weight to 1·75 kgm., and the density is 1·22. It contains about 43 per cent. of HCl; the commercial acid contains about 40 per cent., its density being 1·20.

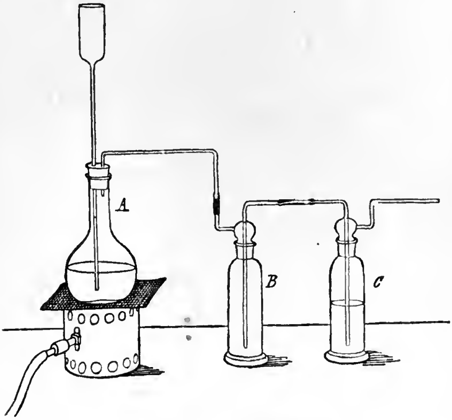


FIG. 125.—Preparation of Hydrogen Chloride.

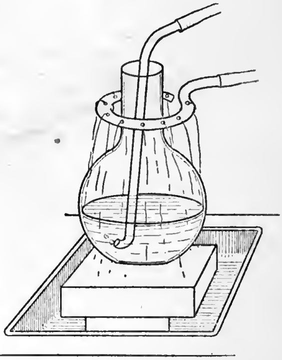


FIG. 126.—Preparation of a Solution of Hydrogen Chloride.

Densities of aqueous solutions of hydrochloric acid at 15°.

Density.	Per cent. HCl.	Density.	Per cent. HCl.
1·0491	10	1·1490	29·35
1·0784	15·84	1·1696	33·39
1·1014	20·29	1·1901	37·23
1·1271	25·18	1·2002	39·15

The most convenient method of obtaining the gas is to drop concentrated hydrochloric acid into concentrated sulphuric acid by means of a tap-funnel. A rapid stream of gas is evolved.

EXPT. 103.—The great solubility of hydrochloric acid gas in water may be demonstrated by the fountain experiment. A large round-bottomed flask is filled with the gas and fitted with a rubber stopper carrying a tube drawn out inside the flask into a jet. The flask is inverted and connected with a tube dipping into water coloured with blue litmus contained in a second large flask, as shown in Fig. 127. By blowing into the short tube on the second flask a drop of water is forced into the upper flask. The gas is instantly dissolved, and a vacuum is formed. The water in the lower flask is therefore driven in the form of a fountain into the upper flask, and the litmus is turned red by the acid solution formed.

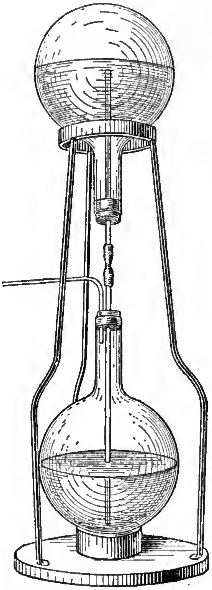


FIG. 127.—Demonstration of the Solubility of Hydrogen Chloride.

EXPT. 104.—Hydrochloric acid collected in jars will be found to extinguish a taper, and to be non-inflammable. Burning sulphur and phosphorus are extinguished in the gas, but a little potassium burning in a deflagrating spoon continues to burn in the gas. If the potassium is heated in a hard glass tube in a current of the gas, it burns, forming potassium chloride, and the hydrogen evolved may be ignited: $2HCl + 2K = 2KCl + H_2$.

The composition of hydrochloric acid.—It is easily shown by experiment that hydrochloric acid gas contains half its volume of hydrogen.

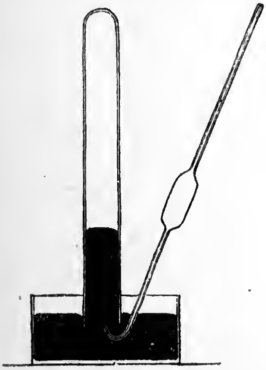


FIG. 128.—Decomposition of Hydrogen Chloride by Magnesium.

EXPT. 105.—Collect the gas in a carefully dried tube over dry mercury (Fig. 128). By means of a bent pipette introduce a drop of water into the tube. The gas at once dissolves, and the mercury rises and fills the tube. Now pass a piece of magnesium ribbon into the tube. It rises through the mercury, and on contact with the aqueous acid dissolves, with liberation of hydrogen. This fills half the tube. If the latter is closed with the thumb, and inverted, the gas may be ignited with a taper: $2HCl + Mg = MgCl_2 + H_2$.

EXPT. 106.—Electrolyse concentrated hydrochloric acid, saturated with common salt, in the apparatus shown in Fig. 129, using electrodes of gas-carbon, since chlorine attacks platinum. The chlorine evolved at the anode at first dissolves in the liquid, but when the latter becomes saturated, equal volumes of hydrogen and chlorine are evolved. These may be recognised by the inflammability of the former, and the action of the latter on a piece of moist litmus paper, which is bleached.

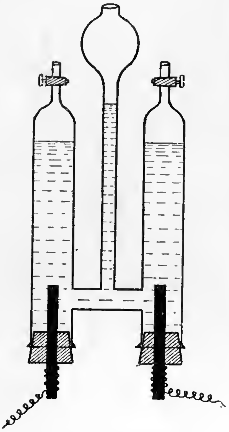


FIG. 129.—Electrolysis of Hydrochloric Acid.

EXPT. 107.—Fill the closed limb of the **U**-tube shown in Fig. 130 with dry hydrogen chloride to the lower stopcock, by admitting the gas through the upper stopcock, and running out the *dry* mercury from the tube. Close the lower stopcock, pour out the mercury, and replace it with liquid sodium amalgam. Open the stopcock, agitate the gas with the amalgam, and allow the apparatus to stand. A white crust of sodium chloride is formed, and the volume of the gas, after levelling, is found to be diminished to one-half. Pour mercury into the open limb of the **U**-tube, and displace the gas through the stopcock. It will be found to be inflammable, and is hydrogen.

EXPT. 108.—Fill one half of a strong glass tube, provided with three stopcocks, as shown in Fig. 131, with chlorine by passing the gas through whilst the middle, three-way, stopcock is open to the air. Fill the other half with hydrogen in the same way. Take the tube into a room with diffused daylight, open the middle stopcock, and allow the gases to mix. After exposure to diffused daylight for a few hours, the greenish-yellow colour of the chlorine disappears. If one of the end stopcocks is opened under mercury, no gas escapes and no mercury enters, hence the volume is unchanged. If the tube is opened under water, the latter enters and fills the tube. The liquid is acid, and contains hydrochloric acid. This experiment shows that 1 *vol. of hydrogen* + 1 *vol. of chlorine* = 2 *vols. of hydrogen chloride*.

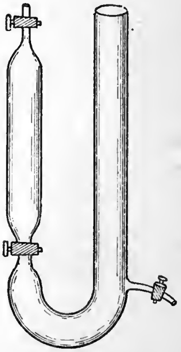


FIG. 130.—Decomposition of Hydrogen Chloride by Sodium Amalgam.

EXPT. 109.—Pass the mixture of hydrogen and chlorine evolved by the electrolysis of concentrated hydrochloric acid, saturated with common salt (Fig. 134), through a glass tube fitted with two stopcocks and platinum firing wires (Fig. 132). The electrolysis should be allowed to proceed for about half an hour before collecting the gas, so as to saturate the liquid with chlorine, and the tube filled in a dark room with a photographic ruby lamp. Support the tube in a clamp behind a strong glass screen, and explode the gas by a spark from a coil. When the tube is cool, open one stopcock under mercury. No gas bubbles out, and no mercury is drawn in, hence the volume is unchanged by combination. Pour a layer of previously boiled water over the mercury and raise the tube so that the open stopcock dips into the water. The gas dissolves, and the tube is filled with water.

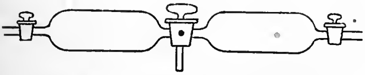


FIG. 131.—Tube for Combination of Hydrogen and Chlorine.


FIG. 132.—Explosion Tube for Hydrogen and Chlorine.

These experiments prove that **1 volume of hydrogen combines with 1 volume of chlorine to produce 2 volumes of hydrogen chloride.** The (corrected) relative density of hydrogen chloride is 18·1, hence its **molecular weight** is 36·2. Thus, 22·2 litres at S.T.P. weigh 36·2 gm. This volume contains 11·1 litres, or 1 gm. of hydrogen, and therefore 36·2 − 1 = 35·2 gm. of chlorine. The formula is HCl_x. But in all the volatile compounds of chlorine, never less than 35·2 parts of chlorine are contained in a molecular weight, hence 35·2 is the atomic weight of chlorine, and the formula of hydrogen chloride is HCl. From the density of chlorine gas, 35·2, its formula is found to be Cl_2.

The atomic weight of chlorine.—By a careful determination of the **limiting density** (p. 147) **of hydrogen chloride,** F. W. Gray and P. F. Burt (1909) found the molecular weight to be 36·187 (H = 1). Hence, the **atomic weight of chlorine** = 36·187 − 1 = **35·187.** By decomposing the gas with heated aluminium they found that 2 vols. gave 1·0079 vols. of hydrogen at S.T.P.

The **gravimetric composition of hydrogen chloride** was directly determined by Dixon and Edgar (1905), who burnt pure hydrogen from a weighed palladium bulb, in pure chlorine from a bulb of liquid chlorine prepared by the electrolysis of silver chloride, and passed into a previously evacuated glass bulb (Fig. 133), the gases being ignited by a spark. The hydrogen chloride was absorbed in water in the bulb, and the residual hydrogen (used in excess) pumped out. The value **Cl = 35·189** was found. Edgar (1908) omitted the water (which gave a little oxygen when chlorine was used in excess), and condensed and weighed the dry hydrogen chloride in a nickel-plated steel bomb, which was placed in liquid air. The hydrogen, chlorine, and hydrogen chloride were all weighed and the synthesis was therefore complete. He found **Cl = 35·187,** which is the accepted value.

Union of hydrogen and chlorine under the influence of light.—A mixture of practically equal volumes of hydrogen and chlorine, containing a minute trace of oxygen, is obtained by the electrolysis of concentrated hydrochloric acid (p. 231). After the electrolysis has proceeded for some time, the gas is passed through a series of very thin glass bulbs (Fig. 134), the whole operation being performed in a dark room lighted by a ruby lamp. The bulbs are then separated and closed by pieces of glass rod inserted into the pieces of rubber tubing. They are preserved in a dark box.

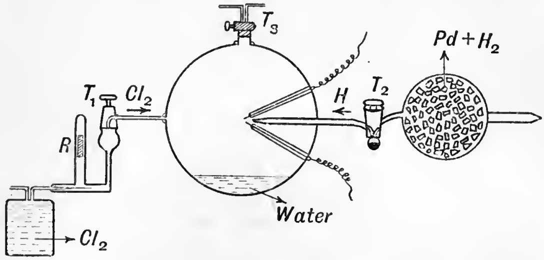


FIG. 133.—Atomic Weight of Chlorine by direct union of Chlorine and Hydrogen.

EXPT. 110.—If a bulb, protected by a screen of plate glass (Fig. 135), is exposed to the light of burning magnesium ribbon, a sharp **explosion** occurs, and the glass is shattered.

The action of **light** in bringing about the union of hydrogen and chlorine is a case of **photochemical catalysis.** Heat is evolved in the reaction, hence the action of light consists only **in initiating the reaction,** which when once started goes on spontaneously (*cf.* p. 695). The action of light in this case is called a **trigger-effect.**

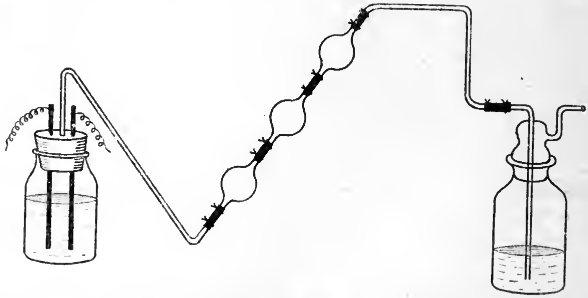


FIG. 134.—Filling Glass Bulbs with a Mixture of Chlorine and Hydrogen.

EXPT. 111.—Break off the tip of a bulb of mixed gases under potassium iodide solution. The latter is coloured brown, owing to liberation of **iodine** : $2KI + Cl_2 = 2K + I_2$, and the liquid rises and half fills the bulb. If the latter is now depressed in water, and the upper capillary broken off, the escaping gas may be ignited : it is hydrogen. Expose another bulb to diffused daylight for a few hours. The colour of the chlorine disappears. Break off the tip of a capillary under mercury.

No gas bubbles out, and no mercury enters. Pour some water coloured blue with litmus over the mercury, and raise the bulb so that the capillary enters the water. The latter fills the bulb and its colour changes to red. Thus 1 vol. of hydrogen + 1 vol. of chlorine = 2 vols. of hydrochloric acid.

Pringsheim (1887) found that if the mixed gases were carefully *dried* with phosphorus pentoxide before passing into the bulb, and the latter exposed to magnesium light, there was no explosion, but only a dull click. The bulb became very hot and the gases were found to have combined completely. (The perfectly dry gases can be exposed to sunlight for several days without complete combination occurring, and without explosion.) Dixon and Harker (1890) found that the velocity of the detonation wave (p. 729) in carefully dried hydrogen and chlorine was 1795 m. per sec.; in the moist gas it was only 1770 m. per sec. Moisture, although assisting the *initiation* of the reaction, therefore appears to retard it once it has begun.

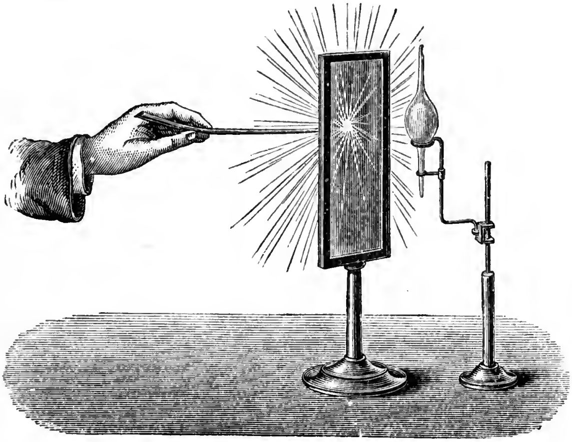


FIG. 135.—Explosion of a Mixture of Hydrogen and Chlorine by exposure to strong light of burning Magnesium.

J. W. Draper (1843) investigated and confirmed an effect noticed by Dalton (1809), that a mixture of *hydrogen and chlorine* did not begin to contract at once when exposed over water to diffused daylight. There was an initial "hesitation," called the **period of photochemical induction,** or **Draper effect.** Bunsen and Roscoe (1857–62) used the apparatus shown in Fig. 136, called an **actinometer,** to investigate the reaction. The mixed gases were confined in the half-blackened flat bulb *i* by chlorine water. On exposure to light, contraction occurred, the HCl formed dissolving, and the rate of combination could thus be estimated by the movement of the thread of liquid in the horizontal tube *k*. It was found that *the rate of combination was proportional to the intensity of the light.* These experimenters also noticed the photochemical induction period.

Burgess and Chapman (1904) showed that the period of photochemical induction was not really peculiar to the reaction $H_2 + Cl_2 = 2HCl$, but was due to traces of impurities, ammonia or nitrogenous organic matter, in the water used to confine the gases. If this water was first boiled with chlorine, these substances were destroyed, and the gases then began to combine the instant they were exposed to light. Traces of oxygen also give rise to a period of induction. The cause of the induction period is not yet clear.

If *moist* chlorine is exposed to light, there is a momentary expansion, due to the heat given out in the reaction: $2Cl_2 + 2H_2O = 4HCl + O_2$ (**Budde effect,** 1871). It is not exhibited by chlorine dried with P_2O_5.

The properties of hydrogen chloride.—Hydrogen chloride prepared from sodium chloride and sulphuric acid is never perfectly pure, but contains traces of sulphuretted hydrogen. The **pure gas** is best prepared by the action of water on silicon tetrachloride (p. 749): $SiCl_4 + 2H_2O = SiO_2 + 4HCl$. Hydrogen chloride is formed by the action of concentrated sulphuric acid on many metallic chlorides, such as those of sodium, potassium, ammonium, calcium, and magnesium—in general, any chlorides which form readily soluble sulphates. Lead chloride, silver chloride, and mercurous and mercuric chlorides are acted upon only with difficulty. Hydrogen chloride is also formed by the action of water on the chlorides of silicon, aluminium ($2AlCl_3 + 6H_2O = 2Al(OH)_3 + 6HCl$), phosphorus, and boron.

FIG. 136.—Actinometer of Bunsen and Roscoe.

The normal density of the gas is 1·63915 gm. per litre. When very strongly heated the gas is slightly dissociated into its elements: $2HCl \rightleftharpoons H_2 + Cl_2$. At 1537°, the dissociation amounts to only 0·274 per cent. (*cf.* steam, p. 212). The gas is also decomposed to a slight extent by radium emanation.

When hydrochloric acid gas is passed through a U-tube cooled in liquid air, it condenses to a snow-white, crystalline **solid,** which melts at $-111·4°$ to a colourless **liquid,** of density 1·184 at the boiling point, $-83·4°$. The perfectly dry liquid is without action on zinc, iron, magnesium, quicklime, and some carbonates, all of which are readily dissolved by the aqueous acid, but it readily dissolves aluminium with evolution of hydrogen: $2Al + 6HCl = 2AlCl_3 + 3H_2$. The liquid expands on heating, between $-80°$ and $+30°$, more rapidly than a gas. The critical temperature of hydrogen chloride is 52·3°; the critical pressure is 86 atm.

Hydrochloric acid is an essential constituent of the gastric juice, occurring to the extent of 0·2 to 0·4 per cent. under normal conditions. It is derived in some way, not understood, from the salt taken with the food.

If a test-tube containing concentrated hydrochloric acid is cooled in liquid air, the acid becomes very viscous and then solidifies, with considerable contraction, to a glassy mass.

On exposure to moist air, the concentrated acid, or the gas, **fumes.** This is due to the attraction of atmospheric moisture to produce a solution which has a lower vapour pressure than water, and is therefore deposited in the liquid state in the form of small drops. In air dried with sulphuric acid, hydrochloric acid does not fume.

Distillation of hydrochloric acid.—When aqueous hydrochloric acid containing 20·24 per cent. of HCl is **distilled,** under 760 mm. pressure, the acid passes over completely without change of composition, as though it were a pure compound. If a weaker acid (*e.g.*, 15 per cent.) is taken, a more dilute acid passes over into the receiver until the residue in the retort contains 20·24 per cent. of HCl, whereas if a stronger acid (*e.g.*, 30 per cent.) is distilled, it loses hydrogen chloride gas with a little moisture until the same 20·24 per cent. acid is left. In both cases the residual acid of 20·24 per cent. HCl then proceeds to distil off without change of composition. Since the composition remains constant during distillation, the vapour has the same composition as the liquid, hence the boiling point (110°) remains constant. This is the **maximum boiling point** for the aqueous acid; both weaker and stronger solutions boil at lower temperatures. The relative numbers of molecules of HCl and H_2O in the liquid of maximum boiling point are $\frac{20{\cdot}24}{36{\cdot}2} : \frac{79{\cdot}76}{18} = 1 : 9{\cdot}94$, or 1 : 10 very nearly. Hence Bineau concluded that the liquid, which certainly seems to behave on distillation like a pure substance (p. 3), was a chemical compound, $HCl,10H_2O$. If this is the case, and it volatilises undecomposed, its vapour-density should be $\frac{1}{2}(36{\cdot}5 + 180) = 108{\cdot}25$; actually it was found to be only about 10, showing that the *vapour* was a mixture: $\frac{108{\cdot}25}{1 + 10} = 10$. It is still possible, however, that the *liquid* is a compound. This was negatived by the experiments of Roscoe and Dittmar (1860), who carried out the distillation under various pressures, and found that **the concentration of the acid of maximum boiling point decreases with the pressure :**

Pressure mm. Hg	50	700	760	800	1800
Per cent. HCl in max. b. pt. acid	23·2	20·4	20·24	20·2	18·2

The composition of a compound would be independent of the pressure over a certain range (possibly limited). It is therefore improbable that

$HCl,10H_2O$ exists even in the liquid; the maximum boiling point acid is a **solution**, and the composition at 760 mm. agrees approximately with a chemical formula only by accident. It may even then be said that the liquid is perhaps a compound which is broken up on heating, but exists at lower temperatures. By passing HCl gas into the concentrated aqueous acid at − 23°, Pierre and Pouchot did obtain a **crystalline hydrate**, decomposing on warming, but it was $HCl,2H_2O$ (m. pt. − 18°), not $HCl,10H_2O$. Rupert (1907) obtained the hydrate HCl,H_2O. There is, therefore, no evidence for the existence of a hydrate $HCl,10H_2O$ boiling at 110°.

The manufacture of hydrochloric acid and chlorine.—On the large scale, hydrochloric acid is made by the action of fairly concentrated sulphuric acid on common salt (**saltcake process**). The acid may be mixed in the gaseous state with air, and the mixture passed over a heated mass containing copper salts, which acts as a catalyst: $4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$ (**Deacon process**). The gas may also be condensed in water in towers, and the solution (**spirit of salt**) decomposed by heating with manganese dioxide: $4HCl + MnO_2 = 2H_2O + MnCl_2 + Cl_2$ (**Weldon process**). Large quantities of chlorine are now prepared directly from common salt by **electrolysis** (p. 296).

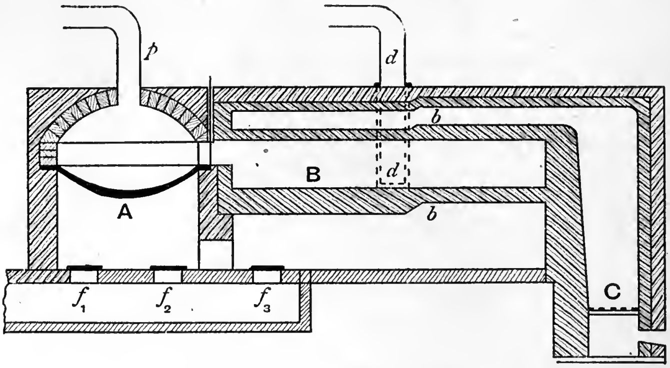


FIG. 137.—Saltcake Muffle Furnace.

The saltcake process.—The first step in the manufacture of caustic soda by the Leblanc process (p. 777) is to decompose common salt with sulphuric acid, with the production of sodium sulphate, Na_2SO_4, known as **saltcake**. The reaction is carried out in two stages. The first stage, which proceeds at lower temperatures, leads to the formation of acid sodium sulphate: $NaCl + H_2SO_4 = NaHSO_4 + HCl$. The second stage is carried out by heating this acid sulphate with common salt, at a dull red heat, when all the acidic hydrogen is expelled: $NaHSO_4 + NaCl = Na_2SO_4 + HCl$.

The operation is carried out in the **saltcake pan** and **muffle furnace** shown in Fig. 137. Half a ton of coarse-grain salt is charged into the large hemispherical cast-iron saltcake pan, *A*, and an equal weight of sulphuric acid, sp. gr. 1·7, run on. A copious evolution of hydrochloric acid occurs, the gas being led off through *p*. When this slackens, the pan is heated by flue gases admitted by means of the dampers, f_1 and f_2. When the first reaction is completed, the pasty mass is raked into the closed box, or **muffle,** *B*, of firebrick, heated externally by flames from the fireplace, *C*, which functions as a gas producer (p. 705). The rest of the hydrochloric acid passes out through the pipe *d*. Saltcake is left in the muffle. A modern furnace produces 85 tons of saltcake per week.

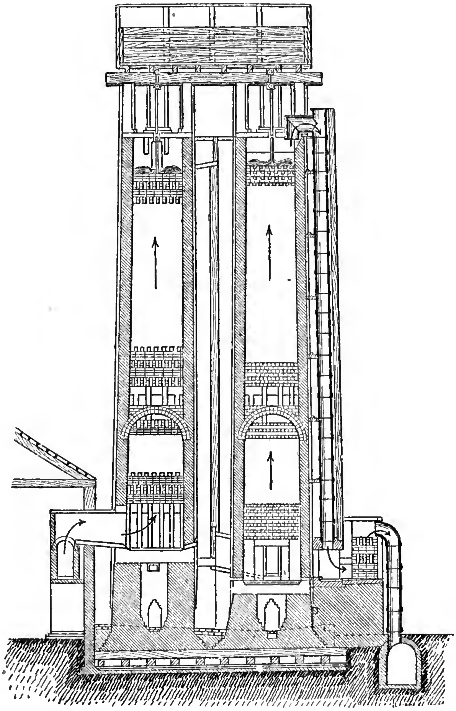


FIG. 138.—Absorption Towers for Hydrochloric Acid.

Hydrochloric acid towers.—The absorption of hydrochloric acid gas in water, which is carried out in the laboratory in Woulfe's bottles, is effected on the large scale in **absorption towers,** introduced by Gossage in 1836. The gas coming from the saltcake furnaces is cooled by passing through a battery of cast-iron pipes (which are not attacked by the gas if the temperature is kept above the point of condensation of the accompanying moisture), and then passes to the base of a tower 60 ft. high, composed of sandstone slabs boiled in tar and clamped together with iron bands, which is packed with lumps of hard coke (Fig. 138). A shower of water is run down, and the hydrochloric acid is almost completely absorbed. To produce strong acid (about 33 per cent. HCl) the liquid is recirculated over the coke packing by acid-pumps of stoneware or ebonite. Efficient absorption depends chiefly on keeping the tower cool, and presenting a large wetted surface to the gas. The latter is provided by the irregularly-shaped lumps of coke, which retains water in its pores.

The manufacture of chlorine by the Weldon process.—Chlorine was formerly made, for producing bleaching liquor, by Berthollet's process, in which **salt** was decomposed by manganese dioxide and sulphuric acid in stoneware jars heated in a water-bath. In 1836, however, Gossage began to condense the **hydrochloric acid,** evolved in the decomposition of salt with sulphuric acid, in towers. Since large quantities of salt were decomposed in the manufacture of alkali by the Leblanc process (p. 777), hydrochloric acid became cheap, and was used as a source of chlorine by treating it with manganese dioxide.

The operation is carried out, on a small scale, in **chlorine stills,** made of flagstones bound together, and having a false bottom *A* on which the lumps of manganese dioxide (pyrolusite) rest (Fig. 139). Hydrochloric acid from the Gossage towers is run on the manganese through the pipe *B*, with a liquid seal below, and the still is heated by admitting steam cautiously from a stoneware column, *C*. Chlorine is evolved through the pipe, *D*, and deposits moisture in the pot shown. The residual liquid in the still contains manganous chloride, ferric chloride (from impurity in the pyrolusite), and a fairly large amount of undecomposed hydrochloric acid.

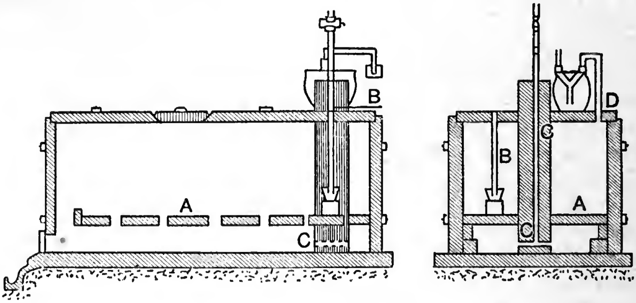


FIG. 139.—Chlorine Still.

In 1837 Gossage attempted to recover the manganese from this liquor, by precipitating it with the theoretical amount of lime: $MnCl_2 + Ca(OH)_2 = CaCl_2 + Mn(OH)_2$. By blowing air through the manganous hydroxide, Gossage hoped to convert it into manganese dioxide, which could be used again: $2Mn(OH)_2 + O_2 = 2MnO_2 + 2H_2O$. He found, however, that the oxidation was very incomplete, and Volhard later pointed out that this was due to the acidic character of manganese dioxide. The latter combined with the manganous oxide, which is basic, to form MnO,MnO_2, or Mn_2O_3, which is very stable. In 1866 Walter Weldon, working at Gamble's alkali works at St. Helens, discovered how to make the Gossage process succeed, and he devised a method for the recovery of the manganese which was for a long time in extensive operation. It is known as the **Weldon process.** Weldon found that if the precipitation of the manganese liquor is carried out in presence of 30–40 per cent. *excess of lime*, then on blowing air through the mixture the manganous oxide is completely oxidised to the dioxide, the latter combining with the lime to form the compounds CaO,MnO_2 and $CaO,2MnO_2$. Lime is a stronger base than MnO, and prevents the latter forming a compound with the MnO_2 and thus escaping oxidation.

An elevation of a Weldon plant is shown in Fig. 140. The acid manganese liquor from the stills is neutralised in the well, *A*, by agitation with limestone, and the ferric hydroxide precipitated is allowed to settle out in the tanks, *B*. The liquor is then pumped into the **oxidiser,** *C*, consisting of a large cylindrical iron tank, where it is treated with the requisite excess of milk of lime. The liquor is heated to 60° by blowing steam into it, and a powerful blast of air is forced through it from a blowing engine. The compound CaO,MnO_2, or **calcium manganite,** is precipitated. More still-liquor is run in, and the blowing continued, when some of the compound $CaO,2MnO_2$ is formed. The suspension from the oxidiser is then run into the settling-tanks, *D*, where a thin black mud, called **Weldon mud,** settles out. The clear liquor, containing calcium chloride, is drawn off and thrown away; the mud (calcium manganite) run down into the octagonal stone chlorine stills, *E*, where it is treated with hydrochloric acid and steam, producing chlorine, and manganese liquor. The latter goes through the Weldon process repeatedly, as described, but fresh manganese dioxide must be added to replace losses. The reactions in the Weldon process are as follows:

1. **Stills** (*E*): (*a*) $MnO_2 + 4HCl = MnCl_2 + Cl_2 + H_2O$ (fresh pyrolusite).
   (*b*) $CaO,2MnO_2 + 10HCl = 2MnCl_2 + CaCl_2 + 2Cl_2 + 5H_2O$ (mud).
2. **Neutralising tank** (*A*): $2FeCl_3 + 3CaCO_3 + 3H_2O = 2Fe(OH)_3 + 3\,CaCl_2 + 3CO_2$.
3. **Oxidiser** (*C*):
   (*a*) *adding lime*: $MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2$.
   (*b*) *air-blowing*: $2Mn(OH)_2 + 2Ca(OH)_2 + O_2 = 2CaO,MnO_2 + 4H_2O$.
   (*c*) *final air-blowing, after adding more still-liquor*:
   $2CaO,MnO_2 + 2Ca(OH)_2 + 2MnCl_2 + O_2 = 2CaO,2MnO_2 + 2\,CaCl_2 + 4H_2O$.

A considerable amount of chlorine is wasted in this process as calcium chloride.

The Deacon process.—The oxidation of hydrochloric acid gas by **atmospheric oxygen** in the presence of a catalyst (EXPT. 85) was applied by H. Deacon and F. Hurter in 1868 as a technical process for the manufacture of chlorine: $4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$. The reaction is reversible; the reverse reaction was described on p. 160. The hydrochloric acid gas, mixed with air, was passed over broken bricks soaked in copper sulphate solution and heated to about 500°. Although chlorine was evolved at first, the reaction soon stopped, and the process, on which great hopes were based, promised to become a complete failure. Hasenclever, in 1883, improved the method, and chiefly in his hands the Deacon process

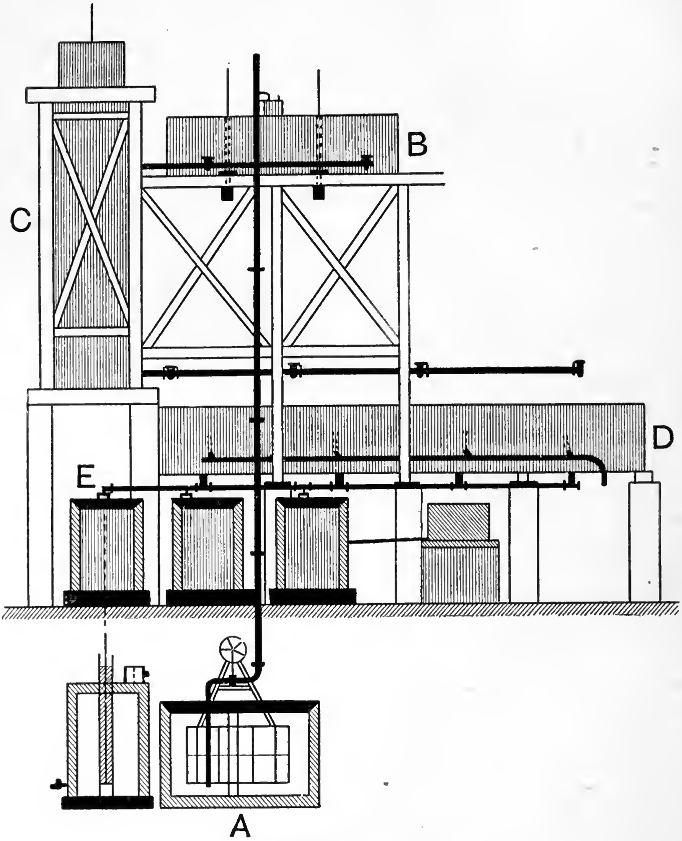


FIG. 140.—Weldon Chlorine Plant.

was converted into a successful technical operation, which almost completely displaced the older and wasteful Weldon process.

Hasenclever found that the contact mass, impregnated with copper salt, lost its activity slowly in any case, and had to be replaced from time to time. He therefore used a container, called a **decomposer,** consisting of an upright iron cylinder, 12–15 ft. wide, containing a ring of broken bricks, previously dipped into a solution of cupric chloride so as to contain 0·6–0·7 per cent. of copper in the mass, supported by iron shutters, and divided into six compartments, one of which can be emptied and refilled with fresh contact mass every fortnight (Fig. 141). The mixture of air and hydrochloric acid gas, 1 vol. of HCl to 4 vols. of air, is passed by a hot Roots' blower through a set of iron pipes heated in a furnace, called a **preheater,** where its temperature is raised to 450°. The gases then pass to the converter, which is kept at this temperature by the hot flue gases from the preheater. About two-thirds of the HCl is decomposed, and the rest is washed out of the gas in a coke-tower with water. The dilute chlorine, containing 5–10 per cent. of chlorine, diluted with nitrogen, is then dried in a sulphuric acid tower, and used in making bleaching powder (p. 376). A diagram of the apparatus is shown in Fig. 142. Hasenclever's main improvement, however, was the preliminary purification of the hydrochloric acid gas. He collected the crude gas from the saltcake furnaces in a Gossage tower, and then ran the aqueous acid in a slow stream into concentrated sulphuric acid, blowing out the hydrochloric acid gas with a current of air. Poisoning of the catalyst was then very much reduced.

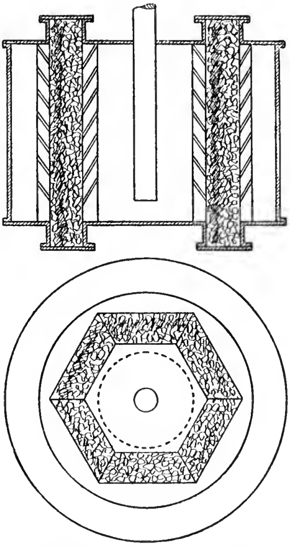


FIG. 141.—Deacon Converter.

The reaction of the Deacon process is **reversible,** and the HCl cannot be completely decomposed. The proportion of decomposition diminishes with rise of temperature, so that the process must be worked at the lowest possible temperature. Below about 350°, however, there is practically no decomposition, and the reaction only becomes sufficiently rapid at 425–450°. We therefore have two opposite conditions to satisfy, (i) the **yield** of chlorine, which *de*creases with rise of temperature; (ii) the **speed** of the reaction, which *in*creases with rise of temperature. A technical balance is struck at about 450°, when about two-thirds of the HCl is decomposed.

When the Deacon process got into complete technical operation, and displaced the Weldon method, it found itself threatened by a new competitor, which will doubtless in time oust the contact process from the field. This is the **electrolytic process,** described in Chapter XVI.

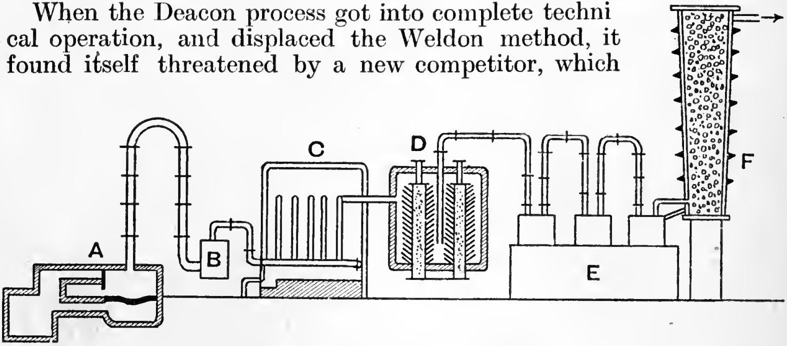


FIG. 142.—Diagram of Deacon Chlorine Plant.

EXERCISES ON CHAPTER XIII

1. Describe the occurrence, manufacture, and properties of common salt. How may (*a*) hydrochloric acid, (*b*) chlorine be prepared from it ?

2. What weight of chlorine would be obtained by decomposing 100 gm. of common salt with manganese dioxide and sulphuric acid ? What volume of water at 15° would be required to dissolve this chlorine ?

3. What experiments would you make in order to demonstrate (*a*) the solubility of hydrogen chloride in water, (*b*) that hydrogen chloride contains half its volume of hydrogen, (*c*) that hydrogen and chlorine combine explosively when exposed to strong light, (*d*) that hydrochloric acid contains chlorine, (*e*) that the bleaching action of chlorine depends on the presence of water ?

4. How are *pure* hydrogen chloride and chlorine prepared ? Describe their properties.

5. Describe the manufacture of hydrochloric acid from common salt. How is chlorine prepared from hydrochloric acid on the large scale ?

6. What is the action of concentrated hydrochloric acid on (*a*) manganese dioxide, (*b*) lead dioxide, (*c*) potassium permanganate, (*d*) potassium dichromate, (*e*) barium peroxide ? Give equations.

6. What views have been held as to the nature of chlorine ? Why is it now supposed to be an element ? Describe, on the assumption that chlorine is oxymuriatic acid, (*a*) the action of manganese dioxide on hydrochloric acid, (*b*) the action of hydrochloric acid gas on heated lead oxide, (*c*) the union of sodium and chlorine.

7. Describe the experiments which have been made on the union of hydrogen and chlorine under the influence of light. How would you prove, by making use of this reaction, that the chemical action of light is proportional to its intensity ?

CHAPTER XIV

VALENCY AND THE STRUCTURE OF COMPOUNDS

Valency.—Hydrogen compounds exist in which one atom of an element is combined with one, two, three, or four atoms of hydrogen:

HCl	H_2O	H_3N	H_4C
Hydrochloric acid.	**Water.**	**Ammonia.**	**Methane.**

The atoms of chlorine, oxygen, nitrogen, and carbon are capable of uniting with one, two, three, and four atoms of hydrogen, respectively. No compound of hydrogen, except hydrazoic acid, HN_3, is known containing more than one atom of an element combined with one atom of hydrogen, and the latter is therefore taken as the standard of **combining capacity** or **valency**. The valency of an element is measured by the number of hydrogen atoms which unite with one atom of that element. Thus chlorine, oxygen, nitrogen, and carbon are **univalent, bivalent, tervalent,** and **quadrivalent** respectively.

Since chlorine is univalent, it may be used instead of hydrogen in determining the valencies of elements. The valencies of elements thus found are the same as those referred to hydrogen, but **quinquevalent** and **sexivalent** elements are now included:

Cl_2O	Cl_3N	Cl_4C	Cl_5P	Cl_6W
Chlorine monoxide.	**Nitrogen trichloride.**	**Carbon tetrachloride.**	**Phosphorus pentachloride.**	**Tungsten hexachloride.**

In the compounds chlorine monoxide, Cl_2O, and calcium chloride, $CaCl_2$, oxygen and calcium are bivalent. When, therefore, calcium and oxygen combine, we should expect them to do so atom for atom, since each of the combining atoms has a valency of two units. This is the case; calcium oxide, or quicklime, has the formula CaO. The valency of calcium may also be inferred from the fact that it can *displace* two atoms of hydrogen, and occupy their place: $2HCl + Ca = CaCl_2 + H_2$. If chlorine is passed over strongly heated lime, one atom of oxygen is displaced by two of chlorine : $2CaO + 2Cl_2 = 2CaCl_2 + O_2$.

There is obviously a close relation between the atomic weight and equivalent of an element and its valency. The **equivalent** is the weight of an element which combines with or displaces unit weight of hydrogen. But the valency is the number of unit weights (atoms) of hydrogen which combine with, or are displaced by, one atomic weight of the element, hence :

$$\textbf{Atomic weight} = \textbf{Equivalent} \times \textbf{Valency},$$

$$\text{or} \quad \text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent}}.$$

Valency volume.—The simplest conception we can form of the displacement of a group of n-univalent atoms from the molecule of a compound by one n-valent atom, *e.g.*, $Al + H_3PO_4 = AlPO_4 + 3H$, is that the n-valent atom occupies the space previously taken up by the n-univalent atoms. This representation will, it is true, be limited to **solid** compounds, because it is only in these that the atoms are in close proximity. Barlow and Pope (1906) found that this relation is true in a number of cases ; they regard the **volume** of an atom as proportional to its **valency,** provided the atoms are arranged in the condition of **closest packing,** although arbitrary assumptions have often to be made which will require further justification.

Oxygen compounds.—If we examine a series of **oxygen compounds** :

Na_2O	(Ca_2O_2)	Al_2O_3	(C_2O_4)	N_2O_5	(S_2O_6)	Cl_2O_7	(Os_2O_8)
Sodium monoxide	**Calcium oxide**	**Aluminium oxide**	**Carbon dioxide**	**Nitrogen pentoxide**	**Sulphur trioxide**	**Chlorine heptoxide**	**Osmium tetroxide**

we see that two additional higher valencies, 7 and 8, appear. Chlorine is **septavalent,** and osmium is **octovalent,** in their highest oxides. (The formulæ of CaO, CO_2, SO_3, and OsO_4 have been doubled for clearness.) The number of atoms of oxygen combining with *two* atoms of an element is a measure of the valency of the latter, since oxygen is bivalent. The valency of 8, shown in the oxygen series, and there only in the compounds osmium and ruthenium tetroxides, OsO_4 and RuO_4, is the highest value ever exhibited. The inactive gases argon, helium, etc., form no compounds with any elements, and their valency is zero. We have therefore, in all, **nine valencies,** shown by various elements, viz., 0, 1, 2, 3, 4, 5, 6, 7, and 8.

Classification of elements according to valency.—We can classify all the elements in **eight groups** (if we exclude zero valency), according to their valencies. The same element may fall into several groups, since it has been shown that the valency may be different, according as the element is combined with hydrogen (HCl, H_2S), or with oxygen (Cl_2O_7, SO_3). These groups are as follows:

0. **Zero-valent elements**: inactive gases, radioactive emanations (p. 463).

I. **Univalent elements**: hydrogen, halogens, alkali-metals, silver, nitrogen in nitrous oxide, N_2O, mercury in mercurous compounds ($HgCl$, Hg_2O), copper in cuprous compounds ($CuCl$, Cu_2O), gold in $AuCl$.

II. **Bivalent elements**: oxygen, nitrogen in nitric oxide, NO, alkaline-earth metals (Ca, Sr, Ba), magnesium, zinc, cadmium, mercury in mercuric compounds ($HgCl_2$, HgO), copper in cupric compounds ($CuCl_2$, CuO), tin in stannous compounds ($SnCl_2$, SnO), lead in plumbous compounds ($PbCl_2$, PbO), iron in ferrous compounds ($FeCl_2$, FeO), sulphur in H_2S, S_2Cl_2.

A large number of elements are seen to be bivalent.

III. **Tervalent elements**: aluminium, boron, nitrogen in NH_3 and NCl_3, iron in ferric compounds ($FeCl_3$, Fe_2O_3), phosphorus in PH_3 and PCl_3, arsenic in AsH_3, $AsCl_3$, As_2O_3, antimony, bismuth, gold in $AuCl_3$.

IV. **Quadrivalent elements**: carbon, silicon, nitrogen in nitrogen dioxide, NO_2, lead in plumbic compounds ($PbCl_4$, PbO_2), sulphur in SO_2, tin in stannic compounds ($SnCl_4$, SnO_2), platinum.

V. **Quinquevalent elements**: nitrogen, phosphorus, arsenic, and antimony in higher halogen or oxygen compounds (N_2O_5, PCl_5, As_2O_5, $SbCl_5$), manganese in manganese trioxide, MnO_3, and manganates, K_2MnO_4.

VI. **Sexivalent elements**: sulphur in SF_6 and SO_3, tungsten in WCl_6.

VII. **Septavalent elements**: chlorine in Cl_2O_7, iodine in KIO_4, manganese in Mn_2O_7, $KMnO_4$.

VIII. **Octovalent elements**: osmium in OsO_4 and OsF_8, ruthenium in RuO_4.

Variable valency.—An element may exhibit a **variable valency** either in its compounds with the *same* element:

PCl_3 (3)	SO_2 (4)	N_2O_3 (3)
PCl_5 (5)	SO_3 (6)	N_2O_5 (5)

or in its compounds with *different* elements:

NH_3 (3)	PH_3 (3)	SH_2 (2)
N_2O_5 (5)	P_2O_5 (5)	SF_6 (6)

It will be noticed that the valency of an element is usually either odd or even, but exceptions are known, *e.g.*, WCl_5 (5), WCl_6 (6), and NH_3 (3), NO (2).

The lowest valency is always shown in the hydrogen compounds, and the highest valency in the oxygen compounds.

If an element, especially a metal, forms two or more series of compounds in which it has different valencies, the properties of the compounds in these series are usually totally different. As an example, we may compare the properties of the ferrous (bivalent iron) and ferric (tervalent iron) compounds :

Ferrous sulphate.	**Ferric sulphate.**
1. Green crystals, $FeSO_4,7H_2O$.	1. White powder, $Fe_2(SO_4)_3$.
2. Greenish-white precipitate with ammonia, $Fe(OH)_2$.	2. Brown precipitate with ammonia, $Fe(OH)_3$.
3. Bluish-white precipitate with potassium ferrocyanide.	3. Dark-blue precipitate with potassium ferrocyanide.
4. Deep blue precipitate with potassium ferricyanide.	4. No precipitate, but dark brown colour, with potassium ferricyanide.
5. No coloration with ammonium thiocyanate.	5. Blood-red coloration with ammonium thiocyanate.
6. Double salt, $K_2SO_4,FeSO_4,6H_2O$, pale green crystals.	6. Double salt, $K_2SO_4.Fe_2(SO_4)_3,24H_2O$, amethyst-coloured crystals.

Unless we knew that ferrous and ferric sulphates were both salts of the same element, iron, the first convertible into the second by boiling with nitric acid, these tests would reasonably lead us to conclude that we had to do with salts of two entirely different elements.

Compounds of an element in which it has a particular valency may resemble compounds of another element of the same valency more closely than they resemble other compounds of the first element with a different valency.

Thus, silver, mercurous, and cuprous chlorides are all white, sparingly soluble solids : AgCl, HgCl, CuCl. Mercuric and cupric chlorides are soluble, and the latter has a green colour. CuCl is therefore more analogous to HgCl and AgCl than to $CuCl_2$. Bivalent lead and tin compounds resemble each other more closely than compounds of bivalent lead resemble compounds of quadrivalent lead, or than compounds of bivalent tin resemble those of quadrivalent tin. Quadrivalent lead and tin are closely analogous :

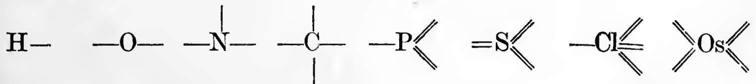
$SnCl_2$	white,	crystalline	solid	$SnCl_4$	colourless,	fuming	liquid
$PbCl_2$	,,	,,	,,	$PbCl_4$	yellow,	,,	,,

In order to distinguish between the various valencies of an element, a Roman numeral representing the valency may be written over the symbol of the atom :

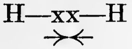
$$\overset{\text{I}}{\mathrm{H}}\quad \overset{\text{II}}{\mathrm{O}}\quad \overset{\text{III}}{\mathrm{N}}\quad \overset{\text{IV}}{\mathrm{C}}\quad \overset{\text{V}}{\mathrm{P}}\quad \overset{\text{VI}}{\mathrm{S}}\quad \overset{\text{VII}}{\mathrm{Cl}}\quad \overset{\text{VIII}}{\mathrm{Os}}.$$

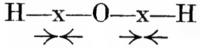
Thus, $H_2\overset{\text{VI}}{S}O_4$ indicates that sulphur in sulphuric acid is sexivalent.

Structural formulæ.—We may form a crude picture of the combination of atoms by assuming that each atom possesses one or more hands, which we represent by **bonds,** or straight lines drawn from the symbol of the atom, as many bonds being drawn as the atom possesses valencies :



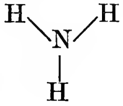
In chemical combination these bonds unite in pairs, *i.e.*, the hand on one bond grasps the hand on another bond :

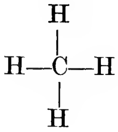




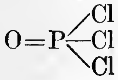
In writing the formulæ of the compounds, the pairs of mutually satisfying bonds are contracted to single bonds :

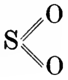
H—H   H—O—H

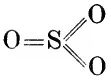




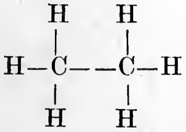
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—H} \\ | \\ \mathrm{H} \end{array}$$





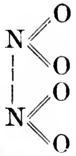


Multivalent atoms are capable of linking with each other, by utilising one or more bonds on each atom ; the remaining valencies are free to attach other atoms :



$$\begin{array}{c} \mathrm{H}\quad\mathrm{H} \\ |\quad\ | \\ \mathrm{H—C——C—H} \\ |\quad\ | \\ \mathrm{H}\quad\mathrm{H} \end{array}$$

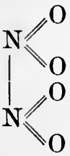
Ethane

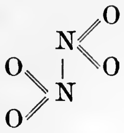


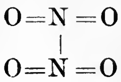
Nitrogen tetroxide

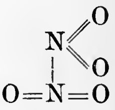
Such formulæ as we have just been using are called **structural formulæ ;** they are supposed to represent the way in which the atoms are united, but not their actual positions, in the molecules.

Thus, the formula for nitrogen tetroxide shows that two nitrogen atoms are united by a single bond, and each nitrogen atom is directly united with two oxygen atoms, in each case by a double bond. But all the following formulæ, which would correspond with different positions in the molecule :



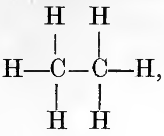






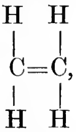
express in this case, where the nitrogen atoms are united by a single bond, exactly the same thing, and are therefore really the same.

Saturated and unsaturated compounds.—In some cases it is assumed that *two* or more valencies of an atom of an element can unite with a corresponding number of an atom of the *same* element :

1. **Ethane,** 

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H,$$

single bond or linkage, between carbon atoms.

2. **Ethylene,** 

$$\overset{\displaystyle H}{\underset{\displaystyle H}{C}}=\overset{\displaystyle H}{\underset{\displaystyle H}{C}},$$

double bond, or linkage, between carbon atoms.

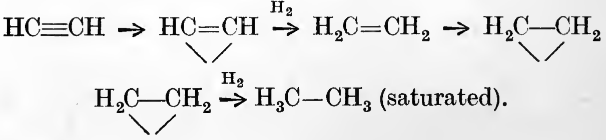
3. **Acetylene,** $H—C\equiv C—H$, **treble bond,** or linkage, between carbon atoms.

Such double and treble bonds are often represented by dots, to save space in printing, thus: $H_3C{\cdot}CH_3$, $H_2C{:}CH_2$, $HC\vdots CH$, which are usually written $CH_3{\cdot}CH_3$, $CH_2{:}CH_2$, $CH\vdots CH$.

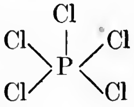
The propriety of this mode of representation is shown by the fact that the molecules of compounds with multiple bonds are **unsaturated,** *i.e.*, they can add on other atoms to form **saturated** compounds :

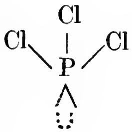
$$CH\vdots CH \xrightarrow{+H_2} CH_2{:}CH_2 \xrightarrow{+H_2} CH_3{\cdot}CH_3.$$

The multiple linkages therefore contain **latent bonds,** each linkage when broken giving *two* available bonds :



It was formerly assumed, and supported by the authority of Kekulé, that variable valency is really always due to latent bonds. Thus, phosphorus was supposed to be always quinquevalent, but in compounds in which it is apparently tervalent two bonds are latent or unsaturated :





Support was lent to this idea by the circumstance, pointed out by Odling, that when the valency of an element changes, it usually does so *two* units at a time. This, however, is not always the case (*cf.* p. 247). The discovery of the stable compound PF_5 (p. 623) entirely vitiated the hypothesis of constant valency.

Valency of radicals.—The conception of valency may be applied not only to the atoms of the elements, but also to the **radicals,** or groups of atoms which take part as a whole in chemical reactions. Thus, in the hydrocarbons ethane, ethylene, and acetylene, we recognise the uni-, bi-, and ter-valent radicals $—CH_3$ (methyl), $>CH_2$ (methylene), and $\overset{\diagdown}{\underset{\diagup}{-}}CH$, respectively. In the same way an inspection of the table :

HNO_3
$NaNO_3$
NH_4NO_3

H_2SO_4
K_2SO_4
$(NH_4)_2SO_4$

H_3PO_4
NaH_2PO_4
Na_2HPO_4

Na_3PO_4
$NaNH_4HPO_4$
$(NH_4)_3PO_4$

leads to the recognition of the following radicals in the compounds :

$$—NO_3,\ >SO_4,\ \overset{\diagdown}{\underset{\diagup}{-}}PO_4,\ \text{and}\ —NH_4.$$

If we know the valencies of the elements and of common radicals, we can at once write down the formulæ of all the salts formed from them.

It is usually most convenient to remember the formulæ of a few typical compounds, from these to deduce the valencies of the elements or radicals, and thence to write down the formula of the compound required.

Thus, if we wish to write down the formula of **aluminium sulphate,** we remember the formulæ $AlCl_3$ and H_2SO_4. Hence we find that Al is tervalent and SO_4 bivalent : $—Al<$, $>SO_4$. In order to satisfy the valencies of Al by those of SO_4, we shall have to take 2Al, *i.e.*, 6 valencies, and $3SO_4$, also 6 valencies. No free valencies must be left over. Hence aluminium sulphate is $Al_2(SO_4)_3$.

The following table contains the valencies of a few common elements and radicals. They are arranged into **electropositive** and **electronegative** groups. The former include elements or radicals which are attracted to the negative pole in electrolysis, the latter comprises elements attracted to the positive pole (Chapter XVI). They are also in the order of the list given on p. 133; metals and hydrogen are electropositive; oxygen and halogens are electronegative; the other elements are sometimes positive and sometimes negative.

In its compounds with hydrogen or metals an element is assumed to be electronegative; in compounds with oxygen, halogens, and sulphur it is electropositive. Negative atoms or groups, especially those containing oxygen, confer **acid** properties: HCl, H_2SO_4.

TABLE OF VALENCIES OF ELEMENTS AND RADICALS.

1. **Univalent** :—
   Positive : H, Na, K, Li, Cu(ous), Hg(ous), Ag, (NH_4).
   Negative : Cl, Br, I, F, (NO_3), (OH), (MnO_4) (in permanganates).
2. **Bivalent** :—
   Positive : Mg, Sr, Ca, Ba, Fe(ous), Sn(ous), Pb, Cu(ic), Zn, Cd, Hg(ic), Cr(ous).
   Negative : (SO_3), (SO_4), (CO_3), (CrO_4), (MnO_4) (manganates).
3. **Tervalent** :—
   Positive : Al, Fe(ic), Cr(ic), As(ous), Sb(ous), Bi, N, B.
   Negative : N, PO_4, AsO_3, AsO_4.
4. **Quadrivalent** :—
   Positive : Si, Sn(ic), Pb(ic), C (in CCl_4).
   Negative : C (in CH_4), Si (in SiH_4).
5. **Quinquevalent** :—
   Positive : N (in N_2O_5), P (in PCl_5, P_2O_5).
6. **Sexivalent** :—
   Positive : S (in SF_6, SO_3), Cr (in CrO_3).
7. **Septavalent** :—
   Positive : Cl (in Cl_2O_7), Mn (in Mn_2O_7, $KMnO_4$).
8. **Octovalent** :—
   Positive : Os (in OsF_8), Ru in RuO_4.

Elements of low valency are either distinctly electropositive or distinctly electronegative (*e.g.*, alkali metals, halogens). This sharp definition of properties falls off as the valency increases; quadrivalent elements have practically no electrochemical character, and are sometimes weakly positive (CCl_4), and sometimes weakly negative (CH_4). Elements of valency higher than 4 are all positive.

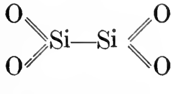
Molecular compounds.—Saturated **molecules** often have the capacity of uniting with each other, although they cannot take up additional *atoms* of elements. Thus, hydrofluoric acid, HF, and potassium fluoride, KF, although both are saturated compounds, combine to form the salt potassium hydrogen fluoride, KHF_2. This salt is readily broken up on heating, into KF and HF, and hence it is usually formulated as KF,HF, as though the separate molecules are contained in it, and called a **molecular compound.**

The explanation of the formation of compounds from apparently saturated molecules is based on the hypothesis of **residual valencies.** The free positive valency of potassium is not quite neutralised by the free negative valency of fluorine when the elements combine atom for atom; in order to bring about complete neutralisation, a fraction of an atom more of fluorine would be required. The addition of this fraction of an atom is impossible, hence the KF molecule exhibits a **residual positive valency.** The electronegative valency of fluorine is not entirely neutralised by the positive valency of hydrogen, hence the HF molecule exhibits a **residual negative valency.** These residual valencies are represented by dotted lines instead of by bonds; they are less than a unit of **free valency** as exhibited by a hydrogen atom: $\overset{+}{\mathrm{K}}\mathrm{F}$ . . . and $\overset{-}{\mathrm{H}}\mathrm{F}$ . . . The two residual valencies, although not capable of uniting with a univalent atom, can unite with each other, forming the molecular compound KF . . . HF. The constituents of molecular compounds are usually separated by commas, *e.g.*, KF,HF.

It is usual to recognise **three kinds of valencies:** (1) **free positive valencies** and (2) **free negative valencies,** exhibited by **atoms** or **radicals**; (3) **residual valencies,** exhibited by **molecules.**

Determination of valency.—The valency of an element in a particular compound can be determined with certainty only (i) from compounds containing a single atom of the element, (ii) if the **molecular weight** of the compound is known, and thence its molecular formula.

Silica, SiO_2, is a non-volatile solid, and its formula may be SiO_2, Si_2O_4, Si_3O_6, . . . or generally, $(SiO_2)_n$. In SiO_2, silicon is quadrivalent: O=Si=O, but in Si_2O_4 it is quinquevalent:



Silicon is assumed to be quadrivalent because the compound $SiCl_4$ is volatile, and its molecular weight can be found. The molecular weight of a substance can also be found in **solution,** p. 299; hence the compound must be volatile, or must dissolve without decomposition in a solvent, in order that its molecular weight can be found. Very complicated formulæ of silicates, for instance, are found in chemical literature, but as the compounds are neither volatile nor soluble, the structural formulæ are guesswork, and have very little scientific value. The presence of certain **groupings of atoms** in a compound may often be inferred from chemical reactions, and in the case of carbon compounds, where the valencies are not usually variable, this may lead to the structural formula of the compound.

Thus, alcohol has the empirical formula C_2H_6O. This is also the formula corresponding with the molecular weight, deduced from the vapour density. One of the hydrogen atoms, however, is in a different relation towards oxygen from the rest, since the action of phosphorus pentachloride, or hydrochloric acid, leads to the formation of the compound C_2H_5Cl, and only one atom of hydrogen is displaced by sodium, forming C_2H_5ONa. The group (OH) in the former reaction has therefore been replaced by the univalent atom Cl, and since with many other compounds the same reaction is exhibited, we assume that one atom of hydrogen in alcohol is present as a **hydroxyl group,** so that the formula must be written $C_2H_5{\cdot}OH$. The compound, C_2H_5Cl, is also produced by replacing one atom of hydrogen in the hydrocarbon ethane, C_2H_6, by chlorine: $C_2H_6 + Cl_2 = C_2H_5Cl + HCl$.

The following formulæ have been found from direct measurements of vapour densities, in some cases (*e.g.*, AgCl at 1735°) at very high temperatures:

NaCl
KCl
KI
RbCl

CsCl
CsI
AgCl
InCl
TlCl

$BeCl_2$
$CrCl_2$
$FeCl_2$
Cu_2Cl_2
Hg_2Cl_2
$ZnCl_2$
$GaCl_2$
$SnCl_2$
$InCl_2$
$HgCl_2$
$PbCl_2$

$AlCl_3$ (above 800°)
$CrCl_3$
$FeCl_3$ (at 750°)
$GaCl_3$

$InCl_3$
$SbCl_3$
$BiCl_3$

$TiCl_4$
VCl_4
$GeCl_4$
$SnCl_4$

$ZrCl_4$
UCl_4

$NbCl_5$
$TaCl_5$
$MoCl_5$
WCl_5

WCl_6

The valencies of the corresponding metals, except in the cases of Cu_2Cl_2 and Hg_2Cl_2, are therefore placed beyond doubt. In many cases the valency has been confirmed by the vapour densities of volatile **organo-metallic compounds:**

$$\text{Zinc methyl } \overset{\text{II}}{Zn}(CH_3)_2. \quad \text{Lead tetraethyl } \overset{\text{IV}}{Pb}(C_2H_5)_4$$

$$\text{Aluminium acetonylacetone } \overset{\text{III}}{Al}(C_5H_7O_2)_3.$$

The valency of an element may be determined from the ratio of the atomic weight to the equivalent, if the atomic weight can be found. In most cases this requires a knowledge of the molecular weight of a series of compounds (p. 143), but sometimes the determination of the **specific heat** of the element in the free state may be used to ascertain the atomic weight. According to **Dulong and**

Petit's law (p. 146), the product of the specific heat and atomic weight of a solid element is constant, and equal to 6·3. If the atomic weight is found in this way, and divided by the equivalent, determined by a particular method, the valency of the element is found.

Thus, the equivalent of zinc, as determined by the amount of hydrogen evolved by the action of 1 gm. of zinc on dilute hydrochloric or sulphuric acid, is 32·5. The specific heat of the solid metal is 0·0955, hence the atomic weight of zinc is approximately $6{\cdot}3 \div 0{\cdot}0955 = 65$. But $32{\cdot}5 \times 2 = 65$, hence the valency of zinc in the chloride and sulphate is 2, and the formulæ of these compounds are $ZnCl_2$ and $ZnSO_4$.

Causes of variation of valency.—The valency of an element may alter as a result of **physical** or **chemical** causes. Thus, phosphorus pentachloride, PCl_5, containing quinquevalent phosphorus, is decomposed by **heat** into phosphorus trichloride, PCl_3, containing tervalent phosphorus : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. PCl_5 is not a molecular compound, as it volatilises almost unchanged in an atmosphere of PCl_3. Mercurous oxide is decomposed by **light** into mercuric oxide and metallic mercury : $\overset{I}{Hg_2}O = Hg + \overset{II}{Hg}O$. Phosphine, PH_3, and hydrochloric acid, HCl, do not combine at ordinary pressure, but under **increased pressure** they give solid phosphonium chloride containing quinquevalent phosphorus : $PH_3 + HCl \rightleftharpoons PH_4Cl$.

Chemical changes often lead to alteration of valency : *e.g.*, according as an excess or deficit of an element or radical is present during the preparation of the compound (*cf.* EXPT. 55) : $2Hg\ (\text{excess}) + I_2 = 2\overset{I}{Hg}I$; $Hg + I_2\ (\text{excess}) = \overset{II}{Hg}I_2$. In some cases only one compound is formed under all conditions from the elements, *e.g.*, tin always forms stannic chloride with chlorine : $Sn + 2Cl_2 = SnCl_4$, even if tin is in excess, but the action of hydrochloric acid leads to the formation of stannous chloride : $Sn + 2HCl = SnCl_2 + H_2$.

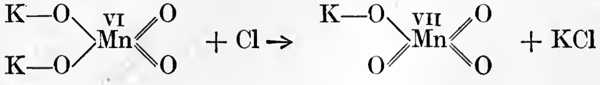
Changes of **oxidation** and **reduction** bring about changes of valency : $Sn \rightarrow \overset{II}{Sn}O \rightarrow \overset{IV}{Sn}O_2$ (oxidation) ; $\overset{III}{Fe_2}O_3 \rightarrow \overset{II}{Fe}O$ (reduction). **Oxidation leads to increase of valency, reduction to decrease of valency.** The change of a ferrous to a ferric salt, for instance, is also called oxidation, because the valency of iron in ferric salts is higher than that in ferrous salts, and the two series of salts may also often be regarded as derived from a higher and lower oxide of iron, respectively :

ferrous sulphate	$\overset{II}{Fe}SO_4$	FeO,SO_3
ferric sulphate	$\overset{III}{Fe_2}(SO_4)_3$	$Fe_2O_3,3SO_3$.

Ferrous chloride, $FeCl_2$, is said to be " oxidised " to ferric chloride,

$FeCl_3$, since an increase in valency results: neither compound contains oxygen.

By passing chlorine through a green solution of potassium manganate, K_2MnO_4, it is *oxidised* to a purple solution of potassium permanganate, $KMnO_4$, and the valency of manganese is raised from 6 to 7:



Removal of an electropositive atom (K) is therefore equivalent to oxidation; addition of an electronegative atom is also oxidation: $\overset{II}{Fe}Cl_2 + Cl \rightarrow \overset{III}{Fe}Cl_3$. The reverse changes are equivalent to reduction.

An example of a complicated **oxidation and reduction occurring simultaneously** is the action of ferrous sulphate on potassium permanganate:

$$2K\overset{VII}{Mn}O_4 + 10\overset{II}{Fe}SO_4 + 8H_2SO_4 = K_2SO_4 + 2\overset{II}{Mn}SO_4 + 5\overset{III}{Fe_2}(SO_4)_3 + 8H_2O.$$

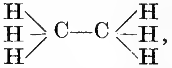
$10\overset{II}{Fe}$ becomes $10\overset{III}{Fe}$, an *increase* of 10 units of positive valency (**oxidation**).

$2\overset{VII}{Mn}$ becomes $2\overset{II}{Mn}$, a *decrease* of 10 units of positive valency (**reduction**).

SUMMARY OF CHAPTER XIV

The **valency**, or combining capacity, of an element is measured by the number of atoms of hydrogen which can combine with one atom of the element. Valencies measured in this way vary from 1 to 4. Oxygen is bivalent (H_2O), but if we examine oxygen compounds we find that elements in them can have valencies from 1 to 8. The inactive gases, since they form no compounds, may be regarded as zero-valent.

Structural formulæ are obtained by linking the atoms (or radicals) so as to satisfy all the valencies in pairs, *e.g.*,



, or $CH_3\cdot CH_3$.

Saturated molecules may combine to form **molecular compounds**; these may be assumed to be formed by **residual valencies**: KF .. HF.

Unsaturated compounds contain **latent valencies**, represented by **double, or treble, bonds,** which can add on univalent atoms in pairs to form saturated compounds: $CH_2{:}CH_2 + Cl_2 = CH_2Cl\cdot CH_2Cl$.

EXERCISES ON CHAPTER XIV

1. Explain what is meant by the statement : "the valency of sulphur in sulphur trioxide is six." What independent evidence is there in support of this ?

2. How is the valency of an element determined ? Of what use is the conception of valency in chemistry ?

3. What is meant by constant valency, varying valency, residual valency, saturated and unsaturated compounds, double linkages, molecular compounds ?

4. Classify the common elements according to valency. Write down the formulæ of bismuth sulphate, aluminium silicate, barium phosphate, calcium permanganate, silicon carbide, ferric phosphate.

5. How may the valency of an element be caused to vary ? What relation does valency bear to oxidation and reduction changes ?

CHAPTER XV

THE MOTION OF MOLECULES

The kinetic theory of gases.—Dalton in 1801 filled two bottles (Fig. 143), one with hydrogen and the other with carbon dioxide, and connected them by a long vertical glass tube, the light gas being above and the heavy gas below. After several hours the gases were found to have mixed uniformly, as may be shown by opening each under caustic soda solution and measuring the absorption. Since the gases have moved in opposition to the force of gravity, this spontaneous mixing of gases, called **diffusion,** must be due to the **motion of the molecules** of the gases amongst each other. This motion in the gases is not perceptible to the eye because the molecules are so very minute.

Similar diffusive motions occur also in **liquids,** but even more slowly. If a tall cylinder is filled with water, and a layer of copper sulphate crystals placed at the bottom (Fig. 144), the salt dissolves, and a blue solution is formed, with colourless water above. If the jar is set aside in a room of uniform temperature, to avoid convection currents, it will be found that the blue colour slowly rises through the jar, until after several months the colour of the solution has become uniform.

We are therefore led to assume that **the molecules of liquids and gases are in ceaseless motion,** in much the same way as a swarm of gnats on a summer evening. This mental picture of the condition of a molecular swarm, as we conceive it to exist in gases and liquids, is called the **kinetic molecular hypothesis** (Greek *kinetos*, motion), or, more briefly, the **kinetic theory.**

From the slowness of diffusive motion it might seem that the **molecular speeds** must be small. This is not correct, and we shall see later that the molecules in air, for instance, are flying about with speeds of the order of a quarter of a mile per second. In the same way the gnats in the swarm are moving about with considerable speeds, although the swarm itself is nearly stationary.

The cause of gaseous pressure.—It was shown by Joule in 1845 that if a gas is allowed to expand into a rigid evacuated vessel, in such a way that it does no external work, it does not become appreciably warmed or cooled. Hence no appreciable work has been done by, or against, possible forces of repulsion or attraction between the molecules, and we must therefore conclude that **the molecules of gases exert practically no forces on one another.**

The **pressure** exerted by the gas uniformly over the walls of the vessel containing it must therefore be wholly kinetic in origin—in other words it must be caused by **molecular bombardment.** On all parts of the surface there is a ceaseless hail of molecules, which impinge on the surface and fly off again into the gas. Without going further into the dynamics of the question one can see that this molecular bombardment, distributed over the surface, must appear to our coarse senses as a uniform pressure.

FIG. 143. Dalton's Experiment on Gaseous Diffusion.

The molecules strike the wall at all angles, from a full normal blow to a glancing impact, and it is evident that it is only the component of the velocity perpendicular, or normal, to the surface which is effective in producing pressure.

In the gas itself the molecules, since they exert practically no forces one upon another, will move in straight lines until they encounter the walls, or one molecule collides with another. These **molecular collisions** will occupy but a small fraction of the whole time in which the molecule is moving, because the particles are sparsely distributed, except in highly compressed gases.

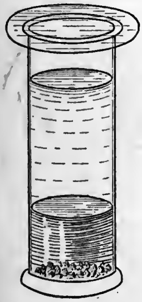


FIG. 144. Liquid Diffusion.

Thus, 1 c.c. of water gives 1240 c.c. of vapour at 100° and 760 mm. pressure, so that less than one-thousandth of the whole space of the vapour is occupied by the volume of the molecules. In air at 0·001 mm. pressure, the molecules occupy only about 1 part in 580 millions of the total space. The gaseous state of matter is therefore one of considerable attenuation.

The molecules can have all possible speeds from zero to infinity, but Clerk Maxwell (1859) showed that the speeds of the vast majority of molecules in a given portion of gas at a given temperature differ only slightly from a **mean speed,** denoted by Ω. The ordinates of the curve in Fig. 145 represent the fractions of the molecules which have speeds represented by the abscissæ.

It will be seen that the numbers of molecules very rapidly become smaller which have speeds deviating appreciably from the mean speed marked off by the vertical ordinate. If we follow *any* molecules along their zigzag paths, we shall therefore find that they all describe these with an almost constant speed, Ω. The *component* velocities are, of course, fluctuating repeatedly, as the molecule undergoes collisions, but the speed along the path of motion is nearly uniform the whole time.

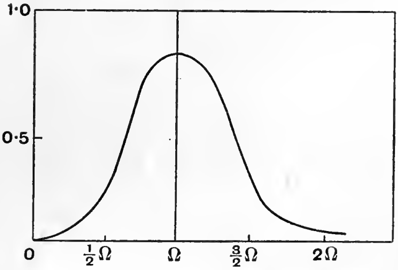


FIG. 145.—Distribution of Molecular Speeds in a Gas.

Calculation of the pressure of a gas.—Consider a mass M grams of a gas, say oxygen, enclosed in a cube of volume v c.c. Let there be n molecules per c.c. of gas, the mass of each being m gm.

Consider a square centimetre of the surface of one of the walls of the cube and suppose that there are n_1 molecules per c.c. with a component velocity u_1 at right angles to this wall, n_2 per c.c. with a component velocity u_2, and so on. Some of these molecules will strike the wall, and rebound from it, and the surface will be subjected to bombardment due to the molecular shower.

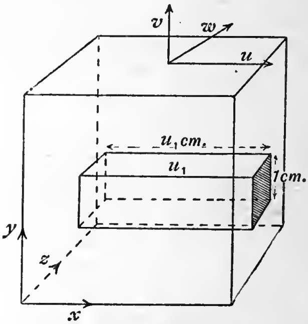


FIG. 146.—Calculation of the Pressure of a Gas from the Kinetic Theory.

Some molecules, however, will be moving away from the wall, and since there is no accumulation of gas in the vicinity of any wall, it follows that, on the average, exactly half the molecules must be moving towards the wall, and the other half away from it. Thus, the number of molecules of the **first type,** *i.e.*, with component velocities u_1, which take part in the molecular shower is $\frac{1}{2}n_1$, and similarly for all the other types.

If we imagine a rectangular box erected on the square centimetre of area as a base, and having a height u_1 (Fig. 146), then all the molecules in this box which are moving towards the wall with velocity u_1 will reach the wall, and be reflected from it, in one second. The reflected molecules move back into the bulk of the gas, and since they will have to pass over a distance greater than u_1, and back again after reflection at the opposite wall, they will not participate again in the molecular shower during the given second of time. The last molecules of the first type to strike the wall will be those at the extreme end of the box, distant u_1, because these can just reach the wall in one second. Molecules farther away will not reach the wall, and this class obviously includes all molecules which have entered the box to replace those leaving it in the opposite direction. We need, therefore, take into account only those molecules present in the box at the beginning of the second of time.

The number of molecules of type u_1 in the box = (vol. of box) × (No. of mols. per c.c.) = $u_1 n_1$, and the number of molecules of the first type which participate in the molecular shower is therefore $\frac{1}{2}u_1 n_1$. Each molecule approaches the wall with velocity u_1 and leaves it, after collision, with velocity $-u_1$. The **momentum** before impact is mu_1, that after impact is $-mu_1$, hence the change of momentum on impact is $mu_1 - (-mu_1) = 2mu_1$. This is balanced by an equal reaction on the wall, directed outwards from the vessel. The total momentum given up to the wall per second by molecules of the first type is equal to (No. of molecules of type 1 striking wall per sec.) × (momentum imparted by each molecule) = $\frac{1}{2}u_1 n_1 \times 2\,mu_1 = mn_1 u_1^2$. In the same way, by considering boxes of lengths u_2, u_3, etc., we can find the total momentum imparted to the wall per second by *all* the molecules. This will obviously be $m(n_1 u_1^2 + n_2 u_2^2 + \ldots)$, which we can write in the form $mn\overline{u^2}$, where $\overline{u^2}$ is the **mean square of the velocities** $u_1, u_2 \ldots$, viz., $\overline{u^2} = \dfrac{n_1 u_1^2 + n_2 u_2^2 + \ldots}{n_1 + n_2 + \ldots}$, where $n_1 + n_2 + \ldots$ is equal to n, the total number of molecules per c.c. The sum of the momenta imparted per second is, however, the **pressure,** p, exerted by the gas on the wall, and since mn = mass of gas per c.c. = **density** D, it follows that $p = D\overline{u^2}$.

The sum of the mean square velocities at right angles parallel to the edges of the cube is defined as the square of the **mean square speed** : $G^2 = \overline{u^2} + \overline{v^2} + \overline{w^2}$. On the grounds of symmetry, we may suppose that $\overline{u^2} = \overline{v^2} = \overline{w^2}$, hence $\overline{u^2} = \frac{1}{3}G^2$.

Thus the **pressure** is equal to $\frac{1}{3}DG^2$, or to $\frac{1}{3}\frac{M}{v}G^2$,

$$\therefore\ pv = \tfrac{1}{3}MG^2 = \tfrac{1}{3}mnG^2.$$

This is **the fundamental equation of the kinetic theory of gases.**

We see that the mass of gas striking the sq. cm. of the wall per second $= \frac{1}{2}m(n_1 u_1 + n_2 u_2 + \ldots) = \frac{1}{2}mn\bar{u} = \frac{1}{2}D\bar{u}$, where $\bar{u}$ is the mean of the velocities normal to the wall, in the molecular shower. It can be shown that $\overline{u^2}$ is *not* equal to $(\bar{u})^2$, but that

$$\bar{u} = \frac{4}{\sqrt{6\pi}}\sqrt{\overline{u^2}} = 0{\cdot}921\sqrt{\overline{u^2}}.$$

Molecular energy.—The **kinetic energy** of a molecule is $\frac{1}{2}mG^2$, hence the equation we have just deduced shows that : **the product of the pressure and volume of a gas is always equal to two-thirds of the kinetic energy of translation of the molecules.** By **kinetic energy of translation** we mean the energy possessed by the molecules in virtue of their translatory motion in straight lines through the gas ; only this part of their energy makes any contribution to the pressure resulting from the molecular bombardment. Energy due to the rotation of the molecules, or the relative motions of their parts (p. 598), is without influence on the pressure.

But from Boyle's law, $pv =$ const. when the temperature is constant, hence **the kinetic energy of translation depends only on the temperature of the gas, not on its volume.** This is equivalent to Joule's law, from which we started (p. 258).

Now put $v = 22242$ c.c., then at *S.T.P.*, $M = \mathbf{M}$, the **gram-molecule** of the gas, and $n = \mathbf{N}$, the **number of molecules in a gram-molecule.** Avogadro's hypothesis shows that the number **N** is the same for all gases ; it is called **Avogadro's number,** or **Avogadro's constant.** We see that *the kinetic energy of translation of the molecules is the same for a gm. mol. of any gas at a given temperature.* For, kinetic energy $= \frac{1}{2}MG^2 = \frac{3}{2}pv$. But v is the same for a gm. mol. of any gas at a given pressure and temperature, and, by Boyle's law, pv is also constant at a given temperature. We can now calculate this **molecular energy.**

At the melting point of ice, $v = 22242$ c.c., $p = 760$ mm. $= 76 \times 13{\cdot}59 \times 980 = 1013130$ dynes per sq. cm.

$$\therefore \tfrac{3}{2}pv = 22242 \times 1013130 \times \tfrac{3}{2} = 3{\cdot}38 \times 10^{10} \text{ ergs.}$$

Thus, the molecular energy of a gram-molecule of any gas at 0°, due to the translatory motion of its molecules, is large enough to raise a weight of about one-third of a ton through one metre.

Molecular speeds.—From the value of the molecular kinetic energy, $\frac{1}{2}\mathbf{M}G^2$, which is the same for all gases, and equal (very approximately) to 34×10^9 ergs at 0°, we can now calculate the squares of the **molecular speeds,** G^2, by division by the molecular weight in grams, **M**, and multiplication by 2 : $G^2 = \dfrac{\frac{1}{2}\mathbf{M}G^2}{\mathbf{M}} \times 2$.

Thus, in the case of oxygen, $\mathbf{M} = 32 \quad \therefore \quad G^2 = \dfrac{34 \times 10^9 \times 2}{32}$,

$\therefore$ the **mean square speed** $G = 46{,}000$ cm. per sec., or 460 m. per sec. The **mean speed,** Ω, is G multiplied by $0{\cdot}921$, *i.e.*, 425 m. per sec. In the case of hydrogen, the mean speed at 0° is 1700 m. per sec.

TABLE OF MOLECULAR SPEEDS AT 0° IN METRES PER SECOND.

Hydrogen, 1700 (1286)
Helium, 1213
Steam, 566·6 (400)
Nitrogen, 455
Oxygen, 425 (317)
Carbon dioxide, 362 (257)
Chlorine, 288
Mercury vapour, 170

It will be observed that the speed of steam molecules ($\mathbf{M} = 18$) is considerably greater than that of oxygen molecules ($\mathbf{M} = 32$); the speeds of hydrogen and helium are very large relatively to those of the other gases, which may explain the small amounts of the former gases present in the atmosphere, since these gases may have diffused into space. A speed of 1700 m. per sec. is 5500 ft. per sec., or more than a mile per sec., *i.e.*, of the order of speed of a rifle bullet. Owing to these high speeds the kinetic energies of the minute fragments of matter which the molecules represent are high, and the pressures due to the molecular shower are thus explained. It is also seen that the molecular speeds are of the same order as, but about 1·3 times greater than, the **velocities of sound** in the gases, given in brackets after the molecular speeds.

Effusion.—The relation $\frac{1}{2}\mathbf{M}G^2 =$ const. shows that **the molecular speeds are inversely proportional to the square roots of the molecular weights:** $G_1 : G_2 :: \sqrt{\mathbf{M}_2} : \sqrt{\mathbf{M}_1}$. Suppose that the sq. cm. of surface of the wall considered on p. 260 to be a little trap-door, which is opened with a vacuum on the other side. The molecular shower streams into the vacuum with a speed equal to the mean molecular velocity normal to the wall: $\bar{u} = 0{\cdot}921\sqrt{\overline{u^2}}$, *i.e.*, inversely proportional to the square root of the molecular weight. This is the phenomenon of **effusion,** studied by Graham. It is not necessary that the gas shall stream into a vacuum; if it is forced by pressure through a small aperture in a plate exposed to the air, the actual speed of effusion is slowed down by collisions between gas molecules and air molecules, but the *relative* rates of effusion of different gases into air are still in the inverse proportion of the square roots of the molecular weights. By means of this result, it is possible to compare the molecular weights of different gases. The apparatus used, devised by Bunsen, is called an **effusiometer.**

EXPT. 112.—A glass cylinder has two marks, m_1, m_2, scratched upon it, and is placed in a cylinder of water (Fig. 147). At the top of the tube is a stopcock, communicating with the free air through a tube closed by a thin platinum plate, in which a hole has been pierced with a fine needle. The tube is filled with gas to a level below the lower mark, m_1, and the tap is opened. The gas streams out through the fine hole, and the time required for the liquid surface to pass from m_1 to m_2 is taken by a stop-watch. The experiment is repeated with a gas of known molecular weight, *e.g.*, oxygen. The ratio of the squares of the times is the ratio of the molecular weights. If mercury is used, a float is fitted inside the tube, having a line marked on its upper end. The time taken for this mark to pass between two marks on the upper surface of the cylinder is noted.

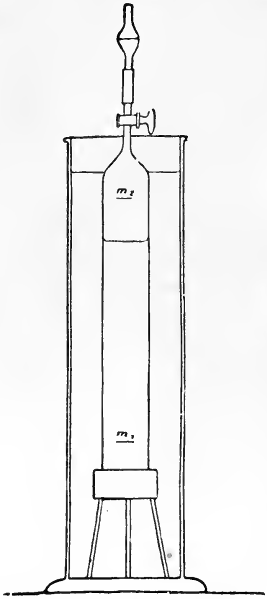


FIG. 147.—Bunsen's Effusiometer (Ostwald).

Absolute temperature.—The product pv for a given weight of gas is proportional to the absolute temperature: $pv = RT$. But pv is proportional to **the translational kinetic energy of the gas molecules,** hence the latter also **is proportional to the absolute temperature.** Since, at constant volume, the pressure increases by 1/273 of its value at 0°C. for 1° rise in temperature, the translational kinetic energy of the molecules must increase by the same fraction of its value at 0°C. In this way we can easily calculate the molecular speeds at any temperature from their values at 0°C. given in the table above.

Thus, the speed of hydrogen molecules at 1000° is found as follows: kinetic energy at 1000° = 1273 × $K.E.$ at 0°C. But the speed is proportional to $\sqrt{K.E.}$

$$\therefore \text{ speed at } 1000^\circ : \text{speed at } 0^\circ = \sqrt{1273} : \sqrt{273}$$

$$\therefore \text{ speed at } 1000^\circ = 1700 \times \sqrt{\frac{1273}{273}} = 1700 \times 2{\cdot}1/6 \text{ m. per sec.}$$

The increase of speed with temperature is therefore not very rapid; it is doubled by a rise of 1000°.

For a gram molecule, $pv = RT$. The kinetic energy of translation of the molecules is $\frac{1}{2}\mathrm{M}G^2 = \frac{3}{2}pv = \frac{3}{2}RT$. The value of R in absolute units (p. 149) is $8{\cdot}25 \times 10^7$ ergs per 1°, hence the kinetic energy at $T°$ absolute is $\frac{3}{2} \times 8{\cdot}25 \times 10^7\ T$ ergs $= 12{\cdot}4 \times 10^7\ T$ ergs. In gram calories, it is $\frac{3}{2} \times 1{\cdot}97\ T = 2{\cdot}95\ T$ gm. cal. $= C_vT$ for a monatomic gas (p. 598).

The molecular diameter.—In spite of the high values of the molecular speeds the diffusion of one gas into another takes place slowly.

Expt. 113.—A small glass bulb containing bromine is placed in a tall stoppered glass cylinder (Fig. 148). The bulb is broken with a glass rod, and a layer of bromine vapour, of a dark red colour, forms at the bottom of the jar. This vapour diffuses only very slowly upwards, although at 17° the speed of the bromine molecules must be

$$1700 \times \left(\frac{300}{273}\right)^2 \times \sqrt{\frac{1}{80}} = 230 \text{ metres per sec.}$$

The actual rate of motion of the bromine vapour is not more than a millimetre per second, or only about one-hundred-thousandth of the molecular speed.

The reason for this difference is, however, clear. The molecules of bromine do not move uninterruptedly in straight lines for indefinite distances; they collide with one another and with the molecules of the air, and a great number of them must be deflected back again to the region from which they started. The molecules describe zigzag paths, and it is only after making a great number of collisions that a molecule can get appreciably forward.

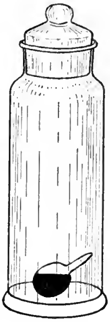


Fig. 148. Diffusion of Bromine Vapour.

The same effect is familiar to us when we walk rapidly into a crowd of people, and if we were thrown back every time we happened to encounter anyone else our progress would be still further impeded.

It is clear that this effect is due to the **finite size of the molecules**; if they were mere points, occupying no space, they would not offer any obstacles to the motions of other molecules. It also appears probable that from the rate of diffusion one should be able to calculate the **diameters of molecules**. Clausius in this way found that the diameter of the oxygen molecule, assumed spherical, is of the order of 10^{-8} cm.

Table of Molecular Diameters in cm. × 10^{-8}.

Hydrogen	2·40	Chlorine	4·96
Helium	2·18	Carbon dioxide	4·2
Oxygen	3·4	Nitric oxide	3·4
Nitrogen	3·5	Steam	4·1

Platinum wires can be drawn to 10^{-4} cm. in diameter; ordinary gold-leaf is 10^{-5} cm. thick; the black parts of soap-films are $6 \cdot 10^{-7}$ cm. thick, and oil-films on water may be only 10^{-7} cm. thick, or even less. The latter contain only a few (less than 10) molecules in the thickness.

The distance of the nearest fixed star is reckoned in light-years, 1 light-year being the distance traversed by light (3×10^{10} cm./sec.) in a year, or 10^{18} cm. It is therefore incorrect to regard the minuteness of molecules as the counterpart of the vast interstellar distances. The molecules are small, it is true—too small to be visible (when their presence would be confusing), but their refinement has not been overdone.

The mean free path.—The mean distance traversed by a gas molecule before collision with another is called its **mean free path,** L. This can be calculated from the **viscosity** of the gas, η, by the formula: $L = 2{\cdot}02\,\eta/\sqrt{pD}$. It is therefore greater the lower the pressure, as is obvious, because then the molecules are less crowded together and their jostling is reduced. In oxygen at S.T.P., L is very nearly 10^{-5} cm.; it is double this in hydrogen.

The mean free path of the hydrogen molecule at atmospheric pressure is equal to the thickness of the thinnest gold-leaf. At low pressures, such as exist in the evacuated spaces of Dewar flasks, the free path is several cm. A molecule rebounds from opposite walls of such a flask many times without encountering another molecule.

During one second a molecule describes as many free paths as it makes collisions, and the sum of the paths is equal to the mean speed Ω. Thus, the **collision frequency,** or the number of collisions per second, $= \Omega/L$. In oxygen, this is $4{\cdot}25 \times 10^4/10^{-5} = 4{\cdot}25 \times 10^9$. At very low pressures the mean free path is 1 cm., but even then there will be 10^5, or 100,000 collisions per second.

The **area** exposed by the surfaces of all the molecules, assumed spherical, in 1 c.c. of oxygen at S.T.P., $4n\pi r^2$, is about 7 square metres.

Molecular magnitudes.—The most important constants in the kinetic theory are: $n =$ the **number of molecules per c.c.** at S.T.P.; $\mathbf{N} = 22242 \times n =$ the **number of molecules in a gram-molecule.** The number **N**, which is the same for all gases, is called **Avogadro's Constant.**

Until quite recently the value of **N** was known only approximately; in some quarters the very existence of molecules was held to be extremely doubtful. Within the last ten years, however, the value of **N**, and hence the absolute mass of a single molecule, have been determined by a variety of methods with an accuracy of about 1 per cent.

The most direct method used in the determination of **N** is due to Rutherford and Geiger. The element **radium** has the property of firing out atoms of helium with extremely high speeds. These atoms, called **α-rays**, move with speeds of about 2×10^9 cm. per sec. (*i.e.*, about 100,000 times faster than gas molecules), and their kinetic energy is therefore extremely large. If the α-rays from a particle of radium, *A*, are allowed to impinge on a screen of zinc-blende, *B*, in the **spinthariscope** of Crookes (Fig. 149), each particle causes a flash of light easily visible under a lens, *C*. It was therefore possible to count the α-rays emitted in a given time, and by collecting the helium from a large amount of radium over a long period, the volume of helium produced from 1 gm. of radium was found to be 0·46 cu. mm. per twenty-four hours. By comparing this with the directly counted number of α-particles (helium atoms) emitted from a known weight of radium in a given time, it was easy to calculate the number of molecules (atoms) per c.c. of helium. This is *n*, and its value came out at **2·7 × 10¹⁹**. Thence **N = 6·05 × 10²³**.

FIG. 149.—Spinthariscope.

A second method used by Rutherford and Geiger (1908) depends on the capacity of the rapidly moving α-particles of rendering a gas through which they pass a conductor of electricity (p. 1021). A long glass tube, *AA′* (450 cm. long and 2·5 cm. wide), called the "firing tube" (Fig. 150), was exhausted, and at the end *A* was placed a preparation of radium on a lead plate, *a*, which expelled α-particles. Some of these were shot along the tube and passed through the narrow tube, *B*, into the brass ionisation chamber *C*, where the gas at low pressure was rendered conducting, or was **ionised.** A mica window at *F* shut off the gas from the evacuated tube, *AA′*. Running axially through the vessel *C*, and insulated from it by the ebonite ends, was a metal wire, *w*, which was connected through a battery and electrometer to the outer surface of the brass vessel. As each α-particle entered the ionisation chamber (at the rate of about one every second), it made the gas conducting, and the electrometer gave a deflection. In this way the individual α-rays

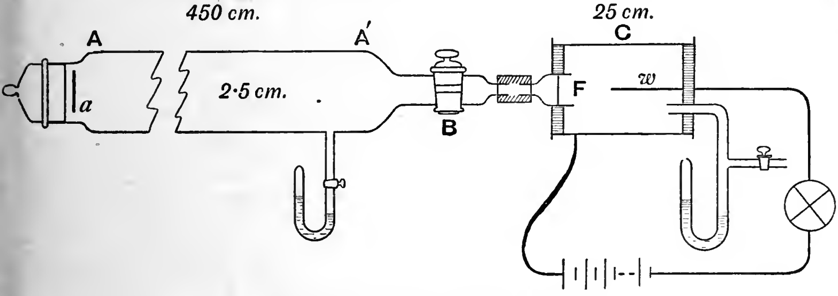


FIG. 150.—Rutherford and Geiger's Apparatus.

were counted, and the method of calculation was similar to that in the first method. The value **N** = **6·09** × **10^{23}** was found.

The determinations of **N** have been made by counting, as above, and from other radioactive experiments, from experiments on colloidal solutions (p. 311), the spectrum, the radiation of heat, the formation of clouds, and the blue colour of the sky. The numbers obtained from the recent experiments are in excellent agreement, and leave no doubt that the latter cannot possibly be the result of chance. Everything points to the **real existence of molecules.** Avogadro's hypothesis may now be regarded as a **law,** and an undue insistence on the hypothetical character of the atomic and molecular conceptions of the structure of matter is belated, and out of touch with modern experimental science. The diversity of methods by which **N** has been found, only a few of which are referred to above, illustrates the fundamental character of the molecular theory in all branches of physics and chemistry.

TABLE OF VALUES OF AVOGADRO'S CONSTANT, **N**.

METHOD.	**N.**
Classical Kinetic Theory	10 × 10^{23} (approximately)
Cloud Formation (p. 1024)	8·3 × 10^{23}
Brownian movement (p. 311)	6·25 × 10^{23}
Radiant heat	6·14 × 10^{23}
Counting α-particles	6·09 × 10^{23}
Electronic charge (Millikan, p. 281)	6·03 × 10^{23}

The most recent measurements agree to within 1 or 2 per cent.

TABLE OF MOLECULAR MAGNITUDES.

Number of molecules per c.c. of gas at S.T.P. $= n = 2{\cdot}70 \times 10^{19}$.

Number of molecules per gram-molecule (22·24 litres in ideal state at S.T.P.) $= \mathbf{N} = 6{\cdot}03 \times 10^{23}$.

Mass of hydrogen atom $= 0{\cdot}000089873/(2 \times 2{\cdot}7 \times 10^{19}) = 1{\cdot}67 \times 10^{-24}$ gm.

Mean speed of hydrogen molecule at 0° $= \Omega_{H_2} = 16{\cdot}94 \times 10^4$ cm./sec.

Translational kinetic energy of a molecule at 0° $= E_0 = 33{\cdot}85 \times 10^9/6{\cdot}03 \times 10^{23} = 5{\cdot}613 \times 10^{-14}$ ergs (p. 262).

Rate of change of translational kinetic energy per 1° $= \epsilon =$

$$5{\cdot}613 \times 10^{-14}/273{\cdot}09 = 2{\cdot}056 \times 10^{-16}\,\frac{\text{erg}}{\text{degree}}$$

A few special magnitudes, not known with the accuracy of the above, may be given for comparative purposes :—

Diameter of hydrogen molecule $= 2{\cdot}17 \times 10^{-8}$ cm.
Mean free path of hydrogen molecules at S.T.P. $= 1{\cdot}42 \times 10^{-5}$ cm.
Average distance apart of gas molecules at S.T.P. $= 3 \times 10^{-7}$ cm
Number of collisions per second of hydrogen molecules at S.T.P. $= 1{\cdot}2 \times 10^{11}$.
Time of describing free path of hydrogen molecules at S.T.P. $= 3 \times 10^{-10}$ sec.

Molecular attraction.—We have assumed so far that the forces exerted by gas molecules on one another are negligibly small. This is only approximately true. Gases are usually more compressible than according to Boyle's law, and this indicates that the molecules attract one another. This **attraction** becomes greater the closer the molecules come together; when the gas is liquefied the molecular attraction is sufficient to prevent the molecules flying off into space, as they do in an open vessel of gas. But a liquid is very much less compressible than a gas, and the compressibility of a gas falls off considerably at high pressures (p. 66). This effect is assumed to be due to the **space occupied by the molecules**, x; if this is comparable with the total space, v, we shall have only the intermolecular space $(v - x)$ available for compression.

These two factors are taken into account by the **equation of Van der Waals.** In this, the ideal gas equation $pv = RT$ is replaced by

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

where a and b are constants: a/v^2 is the molecular attraction correction, which is inversely proportional to the square of the volume; it adds itself to the external pressure: b is the correction for the space occupied by the molecules; according to Van der Waals, b is equal to four times the total volume of the molecules, but it appears to be $4\sqrt{2}$ times the latter. This equation gives very good results with some gases (*e.g.*, ethylene), but there is no doubt that the attraction term depends on the temperature. D. Berthelot has used the equation:

$$\left(p + \frac{a}{Tv^2}\right)(v - b) = RT,$$

with remarkably good results at moderate pressures.

Changes of state.—The attractive forces exerted by molecules upon one another are of considerable magnitude, on account of their propinquity when the substance is in the liquid or solid state. In a liquid we may suppose that the molecules are lying close together, so that there are practically no free paths. The motion of the molecules is now more analogous to gliding of the particles among and over one another.

In the **liquid state** the molecules exert attractive forces on each other, but a molecule in the body of the liquid is attracted equally in all directions, and the resultant force on it is zero. The range of these attractive forces is small; Van der Waals has calculated it to be of the order of 10^{-6} cm. Those molecules lying in the **surface** of the liquid, however, are subjected to a resultant attraction, due to the unbalanced forces of the molecules beneath them, and are under a **pressure** tending inwards towards the body of the liquid (Fig. 151). It is this resultant force which, as is explained in text-books on physics, gives rise to the phenomena of **surface tension.**

Recent investigations appear to lead to the conclusion that the attractive forces between molecules are not exerted uniformly in all directions, but proceed along rays in one or two directions only, as if the molecules were small magnets. The molecules in the surface will then mostly be arranged with the same parts pointing in one direction.

Some of the molecules in the liquid will possess more kinetic energy than the rest, although most of them possess kinetic energies close to a mean value. It may happen that such a molecule, approaching the surface, will have sufficient energy to break away from the attractive forces, and it will proceed outwards into the space above the liquid. This is the phenomenon of **evaporation.**

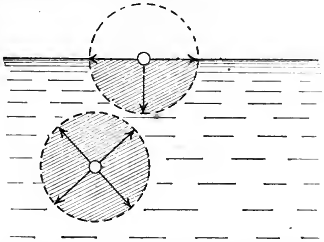


FIG. 151.—Diagram indicating the Range of Molecular Forces in a Liquid.

This escape of molecules of higher kinetic energy than the average will obviously reduce the mean energy of the liquid, which becomes cooler. To maintain the temperature constant, heat must be added from outside; this is the **latent heat of evaporation.**

Molecules in the vapour approaching the liquid will be attracted when they come near the surface. They will then describe curved orbits, and in many cases will be caught by the surface and dragged into the liquid. They experience an acceleration in the field of attraction, and pass into the liquid with increased kinetic energy. Heat is therefore given out on **condensation.** Eventually, a state is reached when as many molecules leap out of the liquid as are dragged back again per second; this is a condition of equilibrium, corresponding with the maximum, or saturation, vapour pressure, but it is a **kinetic equilibrium,** due to two opposite processes, evaporation and condensation, going on simultaneously to equal extents.

In the **solid state** it is assumed that the molecules are fixed in definite positions, each molecule performing oscillations of small amplitude about its position of equilibrium. When heat is imparted to the solid, the amplitude of these oscillations increases, and at a certain temperature the molecules perform oscillations of such amplitude that they collide with each other, and begin to break loose. This is the point of **fusion** at which the solid passes into the liquid state, when the molecules glide about amongst each other. The process of **solidification** consists in the liquid molecules building themselves up again into a system of molecules oscillating about fixed points. The solid molecules exert considerable attractive forces upon each other; in separating them under the influence of these forces work is done, which is equivalent to the **latent heat of fusion.**

The process of rebuilding the solid structure from the liquid takes place around definite points or nuclei. Small crystal aggregates are formed at a comparatively small number of points, and radiating masses of crystals shoot out from these centres until the whole mass is solid. This process can be examined under the microscope, and the appearance is very striking and beautiful. Crystallisation does not usually begin at the freezing point unless solid is present; the liquid must be **supercooled** before solid appears. A solid, on the other hand, always fuses as soon as the melting point is reached, and cannot be permanently superheated. The temperature of the supercooled liquid rises to the melting point when the first portion of solid appears.

At the melting point, when both solid and liquid are present, there is a condition of kinetic equilibrium similar to that described in connection with a liquid in contact with its vapour.

Solution.—When a gas is brought in contact with a liquid, solution occurs until the concentration of gas dissolved in the liquid is in a constant ratio to that in the gas-space, as required by Henry's law (p. 96). A state of equilibrium is set up: Gas $\rightleftarrows$ Gas (dissd.), but there is no reason to doubt that this is a kinetic equilibrium, as in the case of evaporation, the same number of gas molecules entering and leaving the liquid through the surface of separation in unit time.

The mass of gas impinging on the liquid surface per second is $\frac{1}{2}D\bar{u}$ (p. 261) $= \frac{1}{2}D(0{\cdot}921\sqrt{\overline{u^2}}) = \frac{1}{2}D(0{\cdot}921\sqrt{\frac{1}{3}G^2}) = 0{\cdot}266\ DG$. In the case of oxygen at S.T.P., $D = 0{\cdot}001429$ gm. per c.c., $G = 4{\cdot}61 \times 10^4$ cm. per sec., $\therefore$ the mass of oxygen striking 1 sq. cm. of the liquid surface per second is $0{\cdot}266 \times 0{\cdot}001429 \times 4{\cdot}61 \times 10^4$ gm. $= 17{\cdot}5$ gm. This will contain $\dfrac{17{\cdot}5}{32 \times 1{\cdot}66 \times 10^{-24}} = 3{\cdot}3 \times 10^{23}$ molecules, or the number of molecules in about 12 litres.

The molecules striking the surface of the liquid may rebound to a certain extent into the gas-space, but a certain proportion pass through the surface into the liquid, owing to the molecular attraction between the molecules of the gas and those of the liquid.

This is the phenomenon of **solution.** Of the molecules of the gas moving about in the liquid, some will be approaching the surface, and if the kinetic energy of any one of these is above a certain value, it will leave again and pass back into the gas-space. This will occur the oftener the more gas molecules are dissolved. A state of kinetic equilibrium is reached when equal numbers of molecules leap into and out of the liquid per second.

Now let the pressure of the gas be raised. The number of molecules per c.c., or the **concentration,** is increased, and the number striking the surface becomes larger in the same ratio, since it is proportional to D. The number of molecules per c.c. in the liquid is also increased. By reason of this, more molecules leave the liquid than previously. When equilibrium is established, the same number leave as enter, per second, but if the number entering had been increased n times the number per c.c. of liquid will have been increased n times. This is Henry's law.

At first sight it may seem that the gas could have *any* concentration in the liquid, since as many molecules enter as leave. But if we imagine people walking into a room through one door and out through another, so that as many enter as leave, then if they enter twice as fast there will be double the number in the room, although they are also leaving it at twice the previous rate.

The solution of a solid in a liquid may be considered from the same point of view. Molecules are torn away from their centres of oscillation on the surface of the solid, and molecules are caught into positions of oscillation out of the liquid. In this case the kinetic nature of the equilibrium in a saturated solution can be observed, because if an irregular or broken crystal is suspended in a saturated solution, it tends to become more perfect in shape, one portion dissolving and being deposited again in another place.

As to the effect of temperature on solubility, the kinetic theory in its present stage gives no useful information, and we shall omit further description of this subject.

SUMMARY OF CHAPTER XV

The molecules of all bodies, at temperatures above the absolute zero, are in motion. Those of a gas exert practically no forces on each other unless the gas is strongly compressed, and the **pressure** exerted by a gas is due to the bombardment of the walls of the containing vessel by the molecules.

If p is the pressure, D the density, of the gas, the **mean square speed,** G, of the molecules at any given temperature can be calculated from the equation: $p = \frac{1}{3}DG^2$. The **mean speed,** Ω, of the molecules is $0{\cdot}921\sqrt{G^2}$. At 0° the speed of the hydrogen molecule is 1700 m. per sec.; those of other molecules are inversely proportional to the square roots of the molecular weights.

The **kinetic energy** of translation of the molecules in 1 gm. mol. of gas is $\frac{1}{2}\mathbf{M}G^2$, where $\mathbf{M}$ = mol. wt.; this depends only on the temperature and is the same for all gases. At 0° it is $3{\cdot}38 \times 10^{10}$ ergs.

The **velocities of effusion** of two gases are inversely proportional to the square roots of the molecular weights.

The **molecular diameter** is of the order of 10^{-8} cm.; the **mean free path,** *i.e.*, the distance traversed by a molecule before collision, is about 10^{-5} cm. at S.T.P.

Avogadro's constant, N, is the number of molecules in a gm. mol.; with a probable accuracy of 1 per cent. it is $\mathbf{6{\cdot}03 \times 10^{23}}$.

The molecules of liquids and solids are much closer together than those of gases, and exert attractive forces on one another.

EXERCISES ON CHAPTER XV

1. What evidence is there that the molecules of gases and liquids are in motion? What is the speed of hydrogen molecules at 0°? How do you explain the fact that hydrogen diffuses through air at a much slower rate than this?

2. How is the pressure of a gas accounted for on the kinetic theory? Show how the pressure may be calculated from the molecular velocity.

3. What relation is there between the pressure of a gas and the kinetic energy of its molecules? How is the temperature of a gas represented on the kinetic theory?

4. By what methods has the molecular diameter been determined? What is its approximate value, and how near has this been approached in actual bodies?

5. What is Avogadro's constant? How has it been determined?

6. What evidence is there for the existence of molecular attraction (*a*) in gases, (*b*) in liquids? How does the kinetic theory explain evaporation and crystallisation?

7. Show how the effect of pressure on the solubility of a gas may be deduced from the kinetic theory. How would you explain the deviations from the law?

8. 17·91 c.c. of chlorine were mixed with a given volume of oxygen, and allowed to diffuse into a vessel of oxygen for forty-five minutes. 4·05 c.c. of chlorine diffused in this time into the second vessel. The same experiment was carried out with 22·57 c.c. of carbon dioxide, and 6·67 c.c. were found to have diffused in forty-five minutes. Find the ratio of the molecular weights of chlorine and carbon dioxide.

9. What is effusion? How may the molecular weights of gases be compared by their relative rates of effusion?

CHAPTER XVI

ELECTROLYSIS

The dualistic theory of Berzelius.—Lavoisier showed that non-metals (except hydrogen), when burnt in oxygen, yielded **acidic oxides** which produced acids with water. He regarded oxygen as the **principle of acidity** (Greek *oxus*, sour). Davy found that sodium and potassium burnt in oxygen to form **basic oxides,** which gave alkalies with water, hence oxygen is also a constituent of bases. When baryta, or barium oxide, which is a basic oxide, is mixed with the acidic sulphur trioxide, both being solids, the mass becomes red-hot, and the neutral **salt,** barium sulphate, is formed : $BaO + SO_3 = BaSO_4$. Lavoisier considered salts as compounds of acidic and basic oxides, *e.g.*, BaO,SO_3, and this idea of two parts contained in a salt was amplified by Berzelius (1811) into what was called the **dualistic system.**

Berzelius found that solutions of the salts of the alkalies, when decomposed by an electric current, liberated alkali at the negative pole, and acid at the positive pole, and he therefore considered that the alkali and acid possessed positive and negative charges, respectively, and that these were drawn to the poles by the attraction of unlike charges

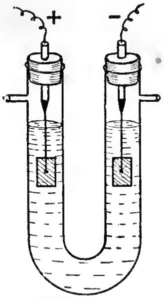


Fig. 152.—**U**-tube with Electrodes.

Expt. 114.—Pour a solution of sodium sulphate, coloured purple with neutral litmus, into a **U**-tube with electrodes (Fig. 152), and connect with the terminals of a battery, or the lighting mains. Observe that the liquid around one (the positive) pole becomes red, showing that an **acid** (sulphuric acid) is set free, whilst that surrounding the other (negative) pole becomes blue, from liberation of **alkali** (caustic soda). Notice also that oxygen and hydrogen are liberated at these poles, respectively.

When a **metal** was deposited, as from copper sulphate, it was supposed to have been formed from the oxide, CuO, by reduction with the hydrogen, which in such cases is not evolved. The hydrogen and oxygen, it was thought, came from the water.

According to the **theory of electrochemical dualism,** salts are **binary compounds** of two oxides, the acid and the base, which are themselves binary compounds of elements with oxygen :

$$\text{Sulphate of soda } \overset{+}{Na_2O},\overset{-}{SO_3}.$$

$$\text{Soda } \overset{+}{Na_2} + \overset{-}{O}. \quad \text{Sulphuric acid } \overset{+}{S} + \overset{-}{O_3}.$$

Elements giving basic oxides were called **electropositive elements,** those giving acidic oxides were called **electronegative elements.** Oxygen was assumed to be always electronegative ; it was " the pole around which the whole chemical system revolved." The gradation of electrochemical character was expressed in the table of elements given on p. 133.

This dualistic system was soon shown to be untenable in its original form. Its downfall was brought about by three circumstances : (1) the recognition of the elementary nature of chlorine, which, since it forms salts, had previously to be regarded as an acidic oxide of an unknown element ; (2) the discovery of the true character of electrolysis, which accounted for the simultaneous production of hydrogen and oxygen in the decomposition of salts ; (3) the investigation of **substitution** reactions in organic chemistry—thus, an electronegative atom of chlorine can replace an electropositive atom of hydrogen without altering very much the chemical nature of the compound (p. 398).

$$\underset{\textbf{Acetic acid}}{C_2H_4O_2} + Cl_2 = \underset{\textbf{Chloroacetic acid}}{C_2H_3ClO_2} + HCl.$$

Many complicated equations involving **oxidations** and **reductions** are, however, most simply written down by making use of the obsolete dualistic notation, and the latter is still of service in this way (p. 969).

The electrolysis of sodium chloride solution.—According to Berzelius's dualistic theory, it might be expected that the electrolysis of a solution of sodium chloride would yield caustic soda and hydrochloric acid. The reaction, however, is different.

EXPT. 115.—Repeat Expt. 114, with a solution of common salt in the **U**-tube. The litmus around the negative pole is turned blue, from liberation of caustic soda, but that around the positive pole is bleached, indicating that chlorine is evolved. Hydrogen is evolved from the negative pole.

It appears that the salt is decomposed with liberation of chlorine, and the sodium first set free at the negative pole then reacts with the water to give caustic soda and hydrogen, which are actually liberated at that pole. The primary production of sodium at the negative pole can, in fact, be demonstrated.

EXPT. 116.—Pour a little mercury into a glass tube having a platinum wire sealed through the bottom (Fig. 153). Fill up the tube with sodium chloride solution, and connect the wire with the negative pole of a battery of two accumulators. The positive pole is connected with a piece of platinum foil dipping into the solution. The liquid soon smells strongly of chlorine, but very little gas is evolved from the mercury. The sodium liberated dissolves in the mercury and forms an amalgam. After a few minutes stop the experiment, and pour the mercury into water. Bubbles of hydrogen are evolved, and the water turns red litmus blue, showing that sodium was present, which reacts with the water.

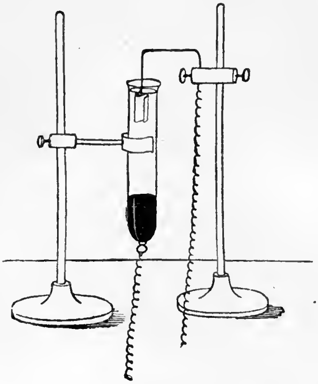


FIG. 153.—Electrolysis Tube with Mercury Cathode.

The sodium chloride in EXPT. 116 is decomposed by the current into sodium and chlorine, which are deposited at the negative and positive poles respectively. The atoms of chlorine combine to form molecules of chlorine gas, which is evolved. The atoms of sodium at once react with the water present, forming caustic soda and liberating hydrogen, which is evolved :

$$\begin{tikzcd}
 & & 2NaCl \arrow[dl] \arrow[dr] & & \\
\textbf{Neg. pole}\ H_2 + 2NaOH & 2H_2O + 2Na \arrow[l] & & 2Cl \arrow[r] & Cl_2\ \text{gas}\ \textbf{Pos. pole}
\end{tikzcd}$$

The **primary products** of the electrolysis are sodium and chlorine ; the sodium reacts with the water to give hydrogen and caustic soda, which are **secondary products**.

J. F. Daniell, of King's College, London, suggested in 1840 that the decomposition of all salts proceeds on the same lines as that of sodium chloride, and that the acid and the base, regarded as primary products by Berzelius, were really secondary products. Sodium sulphate he regarded as a compound of sodium and the radical SO_4, instead of a compound of soda, Na_2O, and sulphuric anhydride, SO_3, so that its formula is $Na_2 \cdot SO_4$. This is decomposed by the current, primarily, into its two radicals, which then react with water to form soda, sulphuric acid, and the two gases hydrogen and oxygen :

$$\begin{tikzcd}
 & & Na_2SO_4 \arrow[dl] \arrow[dr] & & \\
H_2 + 2NaOH & 2H_2O + 2Na \arrow[l] & & SO_4 + H_2O \arrow[r] & H_2SO_4 + O \\
\textbf{Neg. pole} & & & & \textbf{Pos. pole}
\end{tikzcd}$$

All salts were therefore regarded as constituted on the same plan as common salt, whereas the latter was regarded by Berzelius as an exceptional type. This theory was extended by Daniell to the acids ; the latter were regarded as salts of hydrogen. Daniell's theory was shown to be correct, and the dualistic theory of Berzelius was given up.

Electrolysis.—The fundamental laws of electrolysis were discovered by Michael Faraday, whose results were published in 1832. He introduced a number of new names, which are still used in describing the phenomena, and must be mentioned before his conclusions are stated.

Michael Faraday.

Conductors of electricity are of two kinds : (1) those which conduct the current without undergoing chemical change, and are simply heated by the passage of the current ; metals and graphite belong to this class, the members of which are called **metallic conductors :**

(2) those which are decomposed by the current, such as acidulated water, and solutions of salts. Conductors of the second type Faraday called **electrolytes** (Greek *lysis*, setting free). This name is now used to denote the dissolved substances themselves; thus, common salt and sulphuric acid are called electrolytes, because when dissolved in water they form electrolytically conducting solutions. In electrolysis one portion of the products of decomposition travels to the positive pole, or positive **electrode** (Greek *hodos*, an entrance), or **anode** (Greek *ana*, up); the other portion travels to the negative electrode, or **cathode** (Greek *kata*, down). These atoms, or groups of atoms, which wander through the electrolyte Faraday called the **ions** (Greek *ion*, a wanderer); the **anions** are those which appear at the anode, and the **cations** are those which appear at the cathode. A diagram illustrating this nomenclature is shown in Fig. 154. No chemical action is perceptible in the body of the electrolyte, but only at the electrodes.

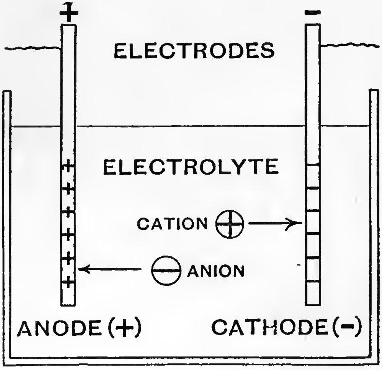


FIG. 154.—Nomenclature of Electrolysis.

Faraday connected in series a number of electrolytic cells, containing different electrolytes, with a battery and an ammeter for measuring the current by its magnetic action, as shown in Fig. 155. Suppose, for instance, that the first cell contains water acidulated with sulphuric acid, the second a solution of copper sulphate, and the third fused stannous chloride. Fused salts are electrolytes, as well as their solutions.

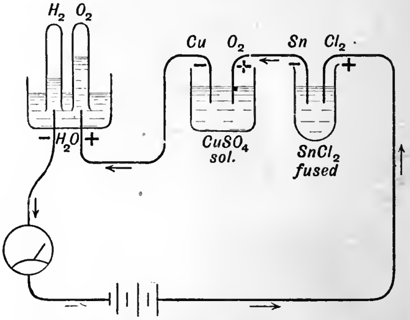


FIG. 155.—Diagram of Electrolytic Circuit.

After the current has passed for a certain time, the products of electrolysis, which are liberated at the electrodes, can be measured. Thus, the volumes of hydrogen and oxygen liberated from the acidulated water, and the weights of copper and tin deposited from the solution of copper sulphate and the fused stannous chloride, respectively, can be ascertained. The quantity of electricity which has passed through the solution is measured by the current strength multiplied by the time. The current strength is measured in amperes, and one **ampere** passing for one second corresponds with unit quantity of electricity, or one **coulomb**. A current of C amperes flowing for t seconds conveys Ct coulombs.

If the current passes until 1 gm. of hydrogen has been liberated from the acidulated water it will be found that 96,000 coulombs of electricity have passed through the cells. Thus, 96,000 coulombs liberate 1 gm. of hydrogen. If this quantity of electricity passes as a small current for a long time (*e.g.*, 0·1 ampere for 960,000 secs.) or as a large current for a shorter time (*e.g.*, 10 amperes for 9,600 secs.), the result is the same. Hence **the weight of an ion deposited in a given time is proportional to the strength of the current.** This is **Faraday's First Law of Electrolysis.**

If the weights of the other ions which are deposited in the cells whilst 1 gm. of hydrogen is liberated in the first are determined, it is found that they are equivalent weights: 7·94 gm. of oxygen, 35·2 gm. of chlorine, 31·5 gm. of copper, and 58·9 gm. of tin. Thus: **96,000 coulombs liberate one gram-equivalent of any ion in electrolysis.** This is **Faraday's Second Law of Electrolysis.**

The quantity of electricity 96,000 coulombs is fundamental in electrolysis, and is called a **faraday,** denoted by **F**. Thus, one **F** liberates 1 gm. atom of a univalent element, and **nF** liberate 1 gm. atom of an n-valent element.

EXAMPLE.—Find the weight of copper deposited from a solution of copper sulphate by a uniform current of 0·25 amp. flowing for one hour.

Quantity of electricity passed through electrolyte $= 0{\cdot}25 \times 60 \times 60 = 900$ cmb.

Copper is bivalent, hence equivalent weight = at. wt. ÷ 2 = 63·1/2 = 31·5.

96,000 cmb. liberate 31·5 gm. of Cu, hence wt. of copper liberated by 900 cmb. $= 31{\cdot}5 \times 900/96{,}000 = 2{\cdot}95$ gm.

Theory of electrolysis.—The **facts** of electrolysis are summarised in the two laws of Faraday. An **explanation** of the phenomena must include these laws. Since the ions are attracted by the electrodes, it is simplest to assume that they are themselves charged, the sign of the charge on an ion being opposite to that of the electrode towards which it moves. Thus, anions are negatively charged atoms or radicals; cations are positively charged atoms or radicals. In the electrolyte we must therefore picture two streams of charged ions moving in opposite directions to the two electrodes (Fig. 156). These streams of charged ions constitute the current in the electrolyte ; the electricity is ferried across from one electrode to the other by the charged ions, and this convective current completes that passing through the metallic circuit outside the cell. The strength of the current is uniform throughout the whole circuit, whether the latter is all metallic, or composed of metal wires and electrolytes. Since the current in the electrolyte is composed solely of charged ions, the weight of the latter moving to the electrodes in a given time is proportional to the current strength. This is Faraday's First Law.

When a positively charged cation touches the cathode, its charge passes into the latter, which is able to conduct the electricity without simultaneous movement of ions. The negatively charged anion touching the anode also gives up its charge, and the two uncharged atoms or molecules are liberated at the electrodes. They may then react with the water to form secondary products.

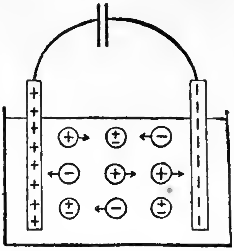


FIG. 156.—Migration of Ions in Electrolytic Cell.

Faraday's Second Law is simply explained by the assumption that the quantity of electricity associated with an ion is the same for all ions of the same valency, and is proportional to the valency. Thus, a univalent cation such as sodium carries one unit charge of positive electricity, a bivalent cation such as copper carries two unit charges of positive electricity, and so on. A univalent anion, such as chlorine, carries one unit charge of negative electricity, which is equal in magnitude but opposite in sign to the charge on the univalent cations, whilst a bivalent anion such as the sulphuric acid radical, SO_4, carries two unit negative charges, and so on.

The ionic charges carry with them the matter with which they are associated. When the ions reach the electrodes, the charges leave them, and the matter is deposited. Since the current is uniform throughout the circuit, the quantities of the ions deposited must all be proportional to the amounts associated with the same quantity of electricity. According to the theory advanced above, these amounts are in the proportion of the chemical equivalents. Thus, the same current deposits amounts of the ions which are proportional to the chemical equivalents. This is Faraday's Second Law of Electrolysis. The quantity of electricity associated with 1 gm. equivalent of an ion is found experimentally to be 96,000 coulombs.

The ionic charges are large. To liberate 1 gm. of hydrogen, the current which lights an electric lamp (0·5 amp.) would have to pass for nearly fifty-four hours. If charges equal to that associated with 1 mgm. of hydrogen could be imparted to each of two small spheres placed 1 cm. apart, they would repel each other with a force of about 10^{10} tons weight. As Faraday remarks, the electric charges concerned in the most violent flash of lightning would barely serve to decompose a single drop of water.

Electrons.—The unvarying amount of the electric charge on univalent ions, and the simple multiple relation between the charges on multivalent ions, suggest at once that electricity, like matter, is divided up into atoms. It might be supposed that there were two kinds of unit charges, one positive and the other negative. A cation would then be an atom or radical plus one positive unit; and an anion would be an atom or radical plus one negative unit. This hypothesis of the atomic structure of electricity originated with Helmholtz (1880): it is a simple outcome of Faraday's results. The view was regarded with scepticism until J. J. Thomson, in 1895, succeeded in actually isolating the unit, or **atom, of negative electricity,** which is called an **electron.** This is the only kind of electricity yet isolated in the free state; a positive charge is always associated with matter, and a positively charged body may thus be regarded as matter which has lost free negative electricity. A negative ion, or anion, is then regarded as an atom or radical plus one or more electrons; a positive ion, or cation, is an atom or radical which has lost one or more electrons. For convenience the charge of an ion is represented by dots or dashes placed over the symbol; one dot denotes unit positive charge, one dash unit negative charge. These symbols are given below on the right.

If the electron is denoted by the symbol ϵ, the constitution of ions may be represented as follows:

chloride ion = chlorine atom + electron = $Cl + \epsilon = Cl'$
hydrogen ion = hydrogen atom — electron = $H - \epsilon = H^{\cdot}$.
ferric ion = iron atom — 3 electrons = $Fe - 3\epsilon = Fe^{\cdot\cdot\cdot}$.
ferrocyanide ion = ferrocyanide radical + 4 electrons = $Fe(CN)_6 + 4\epsilon = Fe(CN)_6''''$.

It has been shown that the electron is material in the sense of possessing a definite mass. This is very small, being only 1/1845 that of the hydrogen atom. The **atomic weight of the electron** is therefore 0·00054. Its **absolute mass** is therefore $0{\cdot}00054 \times 1{\cdot}66 \times 10^{-24} = 8{\cdot}9 \times 10^{-28}$ gm. The radius of the electron has been calculated as $1{\cdot}9 \times 10^{-13}$ cm.

The electronic charge.—Since 1 gm. of hydrogen is associated, in the ionised condition, with 96,000 coulombs of electricity, and since this weight of hydrogen contains $\mathbf{N} = 6{\cdot}03 \times 10^{23}$ atoms, it follows that the value of the unit charge, in coulombs, is $96{,}000/6{\cdot}03 \times 10^{23} =$ **$1{\cdot}592 \times 10^{-19}$ coulombs.**

In calculating from the relation $\mathbf{F} = \mathbf{N}\epsilon$, used above, the value of **F** has been taken as 96,000. This is based on the **International Ampere,** which depends on the deposition of silver from a salt by electrolysis. The international ampere is defined as the current which, flowing uniformly for one second, deposits 0·0011180 gm. of silver. The value of the faraday, **F**, thus depends on the atomic weight of silver. In the International Tables this is given as 107·88 (O = 16), *i.e.*, 107·04 (H = 1). Thus, the value of the faraday will be :

$$\mathbf{F}\,(\mathrm{O} = 16) = 107{\cdot}88/0{\cdot}001118 = 96{,}500 \text{ coulombs ;}$$
$$\mathbf{F}\,(\mathrm{H} = 1) = 107{\cdot}04/0{\cdot}001118 = 95{,}770 \text{ coulombs.}$$

The value 96,000 (H=1) is sufficiently accurate for all practical purposes.

The value of the charge on the electron has been determined in different ways, notably by Millikan, professor of physics at Chicago (1912), who used the following very direct method.

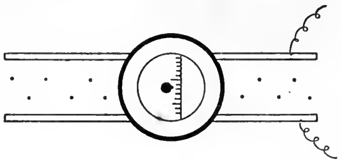


FIG. 157.—Millikan's Determination of the Electronic Charge.

Two metal plates, separated by a distance of about 1 mm., were charged positively and negatively, respectively, by attaching them to the poles of a battery. Into the air between the plates a fine dust of pulverised oil was blown by a spray. The oil drops, which settled very slowly on account of their small size, were found to be electrically charged. A particular drop was focussed in the field of a microscope with a scale in the eyepiece, as shown diagrammatically in Fig. 157. By varying the potential difference between the plates, the charged drop could be made to move upwards or downwards with any desired velocity, or kept suspended. From the difference between the velocities of fall, with and without the potential difference, the charge on the drop could be calculated.

It was found that this charge was not constant, but varied during an experiment. The important thing, however, was that these variations were not continuous, but took place in jumps. Each sudden change was assumed to correspond with the gain or loss of one or more electrons by the drop, and it was found that the charge varied in small multiples of $1{\cdot}59 \times 10^{-19}$ coulombs. Thus, the value of the **charge on the electron** is **$1{\cdot}59 \times 10^{-19}$ coulombs.**

In the above calculation, the value of **N**, which is derived from that of ϵ by the relation $\mathbf{F} = \mathbf{N}\epsilon$, was that found from Millikan's value of ϵ. The values of **N** and ϵ can, however, be determined in other ways. The value of ϵ determined by Rutherford and Geiger, by counting the α-particles emitted from radium (p. 267), was $1{\cdot}55 \times 10^{-19}$ cmb.

Electrolytic dissociation.—The picture of the mechanism of electrolytic conduction employed above implies that the ions move independently through the electrolyte. They behave as if they were free, and each ion responds to the attraction of the electrodes as if the other ions were not present. If the current is switched off, no visible change occurs in the solution, so that we may assume that the ions still remain in the solution free and independent of each other.

Clausius (1857) assumed that in the solution of an electrolyte a few molecules of the salt are broken up into ions, the processes of decomposition and recombination going on continually, and the free ions present at any instant are transported as the current. Williamson (1851) had previously assumed an exchange of atoms between different molecules of the electrolyte, and thought that during the exchange the atoms or radicals existed transitorily in the free state. He assumed, however, that this exchange occurs also in gases. It was Arrhenius, in 1887, who first made the bold assumption that nearly all the molecules of the electrolyte may be dissociated into free ions.

According to this **theory of electrolytic dissociation,** or of **ionisation,** an electrolyte (salt, acid, or base), when dissolved in water or certain other solvents which yield conducting solutions (such as ethyl and methyl alcohols, pyridine, anhydrous hydrocyanic acid, or formamide), undergoes a chemical change in such a way that from the electrically neutral molecule two or more ions are produced. The sum of the positive and negative charges on the ions must always be zero, since the solution as a whole is uncharged.

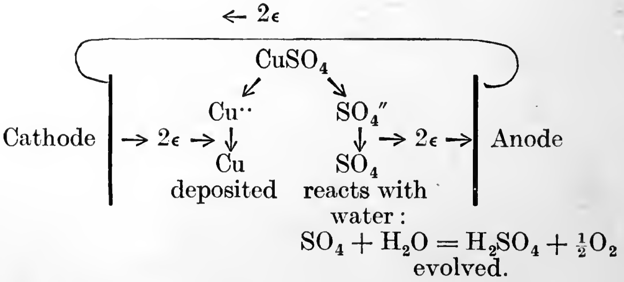
The current in the solution is due solely to the free ions; the undissociated salt molecules do not move to the electrodes. When the ions reach the electrodes their charges are neutralised, and the uncharged atoms or molecules are deposited. The process of electrolysis can, therefore, be represented diagrammatically as in Fig. 156. Thus, sodium chloride, when dissolved in water, is largely ionised into the sodium ion and the chloride ion: $NaCl = Na^{\cdot} + Cl'$. This takes place whether the solution is electrolysed or not. In electrolysis, the negative chloride ions are attracted to the positive anode, and on reaching it give up their charges, becoming chlorine atoms: $Cl' = Cl + \epsilon$. These cannot exist as such, but combine in pairs to form chlorine molecules, which escape as chlorine gas. The positive sodium ions, on reaching the cathode, take from it the negative charges, or electrons, which have passed round the metallic circuit from the discharged chloride ions, and so become neutral sodium atoms : $Na^{\cdot} + \epsilon = Na$. These may dissolve in mercury, if the cathode is metallic mercury; or react with water, forming caustic soda and hydrogen, if the electrode is of platinum.

The atoms of the substances, at the moment of liberation at the electrodes, may be very reactive. Thus, hydrogen liberated by the electrolysis of an acid can bring about the reduction of a ferric salt added to the solution, in the same way as nascent hydrogen (p. 189).

The extent of ionisation of a dissolved electrolyte is called the **degree of ionisation,** and is denoted by α; it corresponds with the degree of dissociation of a gas, γ. Thus α = **ionised part of electrolyte/total amount of electrolyte.** A solution of potassium chloride containing 0·001 gm. mol. per litre is ionised to such an extent that of every 100 molecules of KCl dissolved only 2 remain undissociated and 98 are broken up into ions. The degree of ionisation in this case = 0·98, or 98 per cent.

The ionisation of a dissolved electrolyte is entirely different from the thermal dissociation of a gas. Thus, ammonium chloride on heating dissociates into ammonia and hydrochloric acid : $NH_4Cl = NH_3 + HCl$, but in solution it is electrolytically dissociated into the ammonium and chloride ions : $NH_4Cl = NH_4^{\cdot} + Cl^{\prime}$. It therefore seems expedient to refer to the latter change as ionisation, although this name has recently been used for a different change occurring in gases exposed to X-rays or radioactive substances, and so rendered conductors of electricity (p. 1021).

The reader will have no difficulty in representing the reactions at the electrodes during the electrolysis of salts by means of the ionic theory. The electrolysis of copper sulphate may be taken as an example :



The nature of the ions.—The question at once arises as to how it is possible to have in an aqueous solution of common salt either free sodium or free chlorine, since the former is violently attacked by water, and the latter is a greenish-yellow gas, forming a greenish-yellow solution with water. The solution shows none of the properties of sodium or chlorine. The answer is that neither metallic sodium nor chlorine gas are assumed to be present in the solution, but only sodium ions and chloride ions. These differ from the free elements by possessing large electric charges. It has already been emphasised that ferrous and ferric salts behave like salts of two different elements, and they certainly show none of the properties of metallic iron, except in being slightly magnetic. But these substances must, on the present theory, be considered as giving two different ions in solution, viz., the ferrous ion, $Fe^{\cdot\cdot}$, and the ferric ion, $Fe^{\cdot\cdot\cdot}$. The addition of unit positive charge profoundly alters the properties of the ferrous ion, and it is reasonable to suppose that the sodium and chlorine atoms are also profoundly changed by the assumption of charges by the elements. Metallic sodium, and iron, may be regarded as discharged ions, possessing zero charge, Na°, and Fe°. In converting an atom of iron into a ferrous ion, two electrons are removed, producing $Fe^{\cdot\cdot}$. When this is converted into the ferric ion another electron is removed, producing $Fe^{\cdot\cdot\cdot}$. This, however, corresponds with **oxidation,** since increase of positive valency occurs. Increasing the valency of a cation therefore corresponds with increasing its positive charge. **Reduction** is equivalent to diminution of the positive charge on an ion, or the increase of negative charge. Thus, ferricyanides are reduced to ferrocyanides by increasing the negative charge on the ion by one unit : $Fe(CN)_6''' + \epsilon = Fe(CN)_6''''$. If iron is treated with chlorine water it forms ferric chloride, *i.e.*, ferric ions and chloride ions. The metallic iron has been oxidised : $Fe - 3\epsilon = Fe^{\cdot\cdot\cdot}$, whilst the free chlorine has simultaneously been reduced by acquiring a negative charge: $3Cl + 3\epsilon = 3Cl'$.

The **names of the ions** may be formed from the names of the salts in which they occur, with the addition of -ion.

$Fe^{\cdot\cdot}$, the ion of ferrous salts, is the **ferrous-ion.**
$Fe^{\cdot\cdot\cdot}$, the ion of ferric salts, is the **ferric-ion.**
Cl', the ion of chlorides, is the **chloride-ion.**
SO_4'', the ion of sulphates, is the **sulphate-ion.**

The **hydrogen-ion, $H^{\cdot}$,** is the ion common to all acids ; the **hydroxide-ion,** OH', is the ion common to all bases.

Difficulties in the ionic theory.—The hypothesis of electrolytic dissociation has still to explain how the charged atoms of, say, sodium chloride are separated against the electrostatic forces existing between them. Energy must be available from some source to effect this separation, and the most reasonable assumption seems to be that the ions are drawn apart by their attraction to molecules of the solvent. This separation, as Larmor pointed out, must in some way be effected by a steady drawing apart of the ions of each molecule by attractive forces, the process being reversible as regards each separate molecule, so that there is no violent disturbance, leading to vibration and conversion of energy into heat. The actual **mechanism of ionisation,** however, is still far from clear.

Another criticism advanced against the theory was that, if the ions are free in the solution, it should be possible to separate them. The answer to this is that such a separation can, in fact, be made. If a layer of pure water is poured over a solution of hydrochloric acid, the hydrogen-ions, which move more rapidly than the chloride-ions, as we know from conduction experiments, and from direct measurements of the speeds of ions in a potential gradient (p. 288), will diffuse into the water. Since, however, they carry positive charges, they will charge the water layer positively, and leave the negative chloride-ions in the layer of acid, which thus becomes charged negatively. By reason of the great electrostatic forces soon set up, the hydrogen-ions tend to be dragged back into the acid, and the chloride-ions to be pulled out, so that in a short time both ions migrate together with equal speeds, and the acid appears to diffuse as a whole. The existence of the electrical charges may, however, easily be seen by placing platinum wires in the water and in the acid, and connecting these with a galvanometer. A current flows from the water to the acid. If a non-electrolyte, such as sugar or alcohol, is used no trace of current can be detected.

It is not claimed that the theory of electrolytic dissociation is free from grave difficulties. These are, however, not more numerous than those associated with any purely chemical theory, such as that of the structure of organic compounds, and the theory of the constitution of benzene in particular. They are not the simple difficulties which arise on a first acquaintance with the theory, such as that discussed above, all of which are capable of ready explanation, although they are still sometimes brought up against the theory. What can fairly be claimed for the theory is that it has been, and still is, a valuable and illuminating guide to research, and that it affords a consistent and simple explanation of a large number of experimental results which otherwise would be obscure and disconnected. All the other hypotheses proposed in its place cover a much more restricted field, are without exception qualitative, and in many cases incapable of experimental test. They are, and have shown themselves to be, impotent in assisting the real progress of scientific investigation. The great advances made in physics, notably in connection with the elucidation of the source of the electric current in voltaic cells, must also be kept in view. It may fairly be said that if the theory were abandoned by chemists its position in physics would still be assured.

The ionisation of water.—The purest water which can be obtained is almost, but not quite, a non-conductor of electricity. After allowing for the effects of traces of conducting impurities, a slight conductivity, due to the ions of water itself, remains. The **ionisation of water** into hydrogen-ions and hydroxide-ions is very small, and a state of equilibrium is set up: $H_2O \rightleftharpoons H^{\cdot} + OH'$. To pass a current of 1 ampere through a centimetre cube of pure water at 18° would require a potential gradient of about a million volts, *i.e.*, the electrodes would have to be connected with 500,000 accumulator cells in series.

The ionisation of water proceeds only to the extent of 1 gm. mol. of water ionised in ten thousand million litres (10^{10} litres), or about one-fortieth the total capacity of the earth.

Salts are electrolytes.—If 1 gm. mol. of hydrochloric acid is dissolved in water so that the total volume of solution is 1 litre, the conductivity of the water is increased nearly a thousand million-fold; 1·2 litres of this solution contain 1 gm. of hydrogen-ions, derived from the dissociation of the acid, whereas 10^{10} litres of water contain 1 gm. of hydrogen-ions derived from the dissociation of the water.

Most **acids, bases,** and **salts,** such as hydrochloric acid, sulphuric acid, acetic acid, caustic potash, lime, common salt, copper sulphate, and alum, give conducting solutions with water, and are **electrolytes** (p. 278). Pure sugar, urea, alcohol, and most organic compounds, however, do not give conducting solutions with water: they are **non-electrolytes.** Since acids may be regarded as hydrogen salts, and bases as salts containing the hydroxide radical, OH, the results described may be summarised in the statement that **salts are electrolytes,** whilst substances which are not salts are non-electrolytes.

All acids give the hydrogen-ion in solution; all bases give the hydroxide-ion. Dry liquefied hydrogen chloride does not redden dry litmus, or act on zinc or marble, and it is almost a perfect insulator. In solution it behaves as an acid, since then the hydrogen-ion is formed.

The hydroxide-ion of bases, when liberated at the anode in electrolysis, decomposes into water and oxygen: $2OH = H_2O + O$.

Migration of the ions.—The bodily transfer of the ions under the influence of an electric field can be demonstrated, and its speed measured, by the apparatus shown in Fig. 158 (Nernst).

Expt. 117.—The **U**-tube is half-filled with a solution containing 0·3 gm. of KNO_3 in a litre of water. By connecting a funnel with the capillary tap below the **U**–tube, a solution containing 0·5 gm. of $KMnO_4$ per litre of water, to each 100 c.c. of which 5 gm. of urea have been added to increase its density, is slowly admitted. The surface of separation between the colourless liquid above and the purple permanganate solution below should be quite sharp. A current of 0·3–0·4 amp. is now passed between the platinum electrodes, from the lighting mains. The purple MnO_4'-ions at once begin to move towards the anode, and the levels alter in the directions shown (Fig. 158). If the former levels are marked by thin strips of gummed label, the change is quite apparent after 10–15 minutes.

It appears from this experiment that the actual speed of movement of the ions in bulk through the solution is very slow. It thus resembles the diffusion of dissolved substances. In both cases the moving molecules enter repeatedly into collision with the molecules of the solvent. The actual **ionic mobilities** present, under a potential gradient of 1 volt per cm., are given below in cm. per sec. (for very dilute solutions, where the influence of ions on one another, or on the un-ionised salt molecules, may be neglected):

$K^{\cdot}$	0·00067	$Ag^{\cdot}$	0·00057	Cl'	0·00068	NO_3'	0·00064
$H^{\cdot}$	0·00326	$Na^{\cdot}$	0·00045	OH'	0·00181	I'	0·0069
		$NH_4^{\cdot}$	0·00066	SO_4''	0·00071		

The ions in their motion are under the influence of two forces: (i) the **driving force** of the potential gradient; (ii) the **viscous resistance** of the solvent. The latter frictional resistance is enormous. In order to pull 1 gm. mol. of potassium ions through the solution with a speed of 1 cm. per sec. it would be necessary to apply to them an aggregate force of no less than 1,500,000 tons (Kohlrausch).

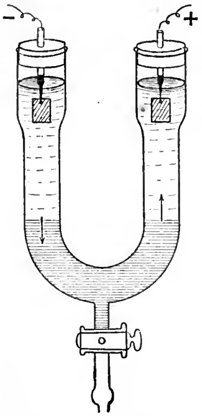


FIG. 158.—Demonstration of Ionic Migration.

Strengths of acids.—Since acids in solution owe their acidic properties to the hydrogen-ion, their **relative strengths** may be compared by measuring the relative ionisations in solutions containing equivalent weights of the acids in identical volumes. The ionisation is most conveniently determined by the **conductivity** of the solution. Since the hydrogen-ion is much more mobile than any of the anions of acids, it carries most of the current, and the relative conductivities of different acids are therefore approximately proportional to the ionisations.

EXPT. 118.—One-fiftieth normal ($N/50$) solutions of acetic, sulphuric, and hydrochloric acids are poured into three glass tubes, fitted with platinum electrodes, as shown in Fig. 159. The electrodes are set at the same distance apart in the three tubes, and in series with each tube is an ordinary carbon-filament lamp. The tubes are connected in parallel with the lighting mains. The lamp in circuit with the acetic acid remains dark, because the conductivity is so small that practically no current passes. The lamps connected with the hydrochloric and sulphuric acids light up, but the former is brighter than the latter. The order of conductivities of the three acids :

$$HCl > H_2SO_4 > CH_3{\cdot}CO_2H,$$

is therefore the same as the order of strengths found by the relative rates of solution of zinc in the acids (p. 184).

Equivalent conductivity.—If a cell is formed containing two platinum electrodes 1 sq. cm. in area, placed parallel to each other at a distance of 1 cm. apart, the current in amperes which passes through a solution of an electrolyte between the plates, when the latter are at a difference of potential of 1 volt, is defined as the **conductivity** of the solution, and is denoted by k. Thus, **conductivity** = **current/voltage** for unit cube of the material.

It is found that the **conductivity of a solution** is very greatly dependent on the **concentration.**

If we start with a solution containing 1 gm. equivalent of electrolyte per litre (*e.g.*, HCl, or KCl, or $\frac{1}{2}H_2SO_4$, or $\frac{1}{2}CuSO_4$), then we shall have a certain number of ions between the electrodes in the cell, and the current carried by these ions will be equal to the conductivity of the solution. If we dissolve twice as much electrolyte in a litre, the actual conductivity will be greater, although there may really be a smaller fraction of salt molecules broken up into ions than in the more dilute solution. Again, if we dilute the solution containing 1 gm. equiv. per litre to one containing 0·01 gm. equiv. per litre, the actual conductivity will be less, as there are fewer ions between the electrodes, although a larger fraction of salt may have been ionised. To make a fair comparison between the ionisations of these various solutions it is evident that we must divide the measured conductivity, k, by the number, c, of gm. equiv. of salt *per c.c.* in the solution, and the quotient k/c is called the **equivalent conductivity**, denoted by Λ. Thus $\Lambda = k/c$.

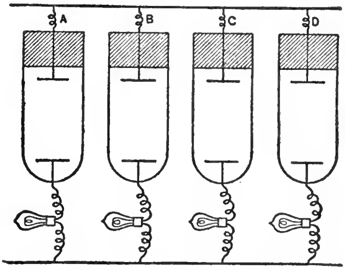


FIG. 159.—Comparison of Conductivities of Acids.

It is found by experiment that the equivalent conductivity of an electrolyte increases gradually with the dilution. The curves in Fig. 160 show the equivalent conductivities of a few electrolytes plotted against the cube-root of the dilution in *litres*. It will be seen that the curves at first rise fairly rapidly, and then slowly approach a nearly constant value at high dilutions.

This is interpreted as follows. The ionisation of the dissolved substance increases with dilution until, at very high dilutions, the electrolyte has become completely ionised. When this occurs, the equivalent conductivity becomes constant, and this limiting value of the equivalent conductivity, corresponding with complete

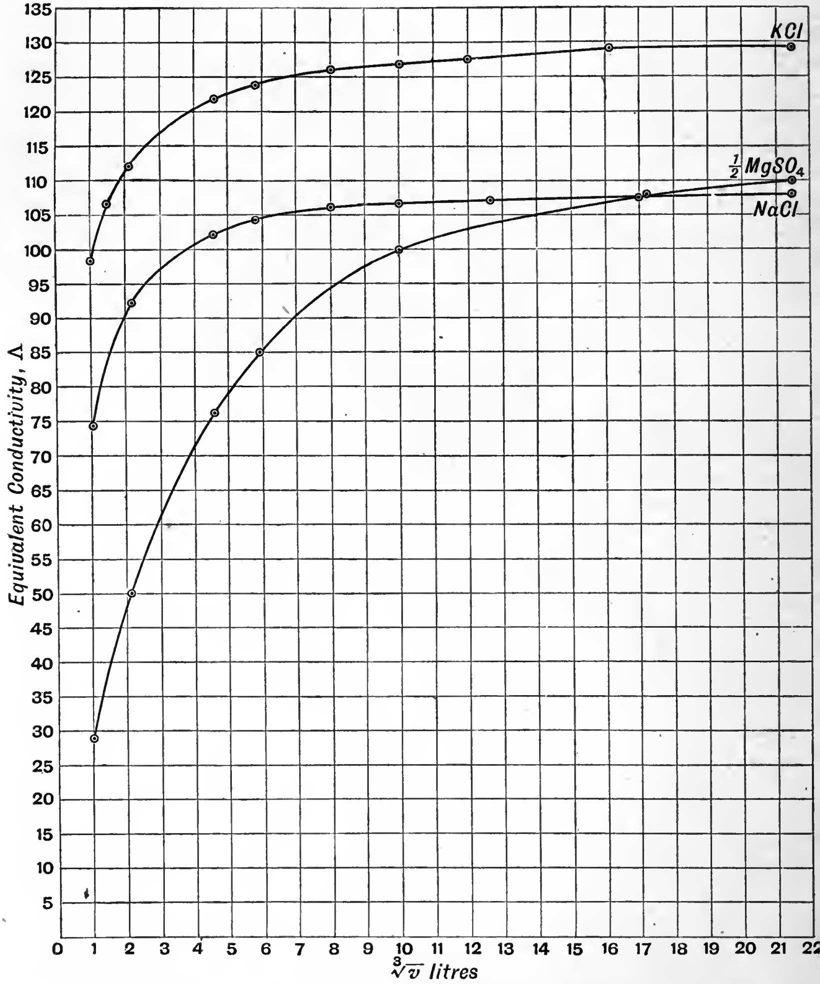


FIG. 160.—Curves showing Dependence of Equivalent Conductivity on Dilution.

ionisation, is denoted by Λ_∞ (*i.e.*, the value at **infinite dilution**). Since there are now only ions in the solution, the ratio k/c, or Λ, has become constant.

Thus, if we have 1 gm equiv in 10^6 litres practically completely ionised, giving a certain conductivity k_1, and we then dilute the solution to 10^{10} litres, we obtain a smaller conductivity, k_2. But if we suppose all the ions present to be collected into 1 c.c. in each case, it is evident that we should have two identical solutions, since the numbers of ions are equal, and thus Λ is the same for both This would not be true except when the salt is *completely* ionised, *i e*, at very great dilutions, because then the number of ions in the two solutions considered would be different, and if we brought them all into 1 c.c. the conductivity in one case would be different from that in the other.

Degree of ionisation.—The ratio of the equivalent conductivity at any dilution, v, to that at infinite dilution, *i.e.*, to the **limiting conductivity** for infinite dilution when all the electrolyte is ionised, is the **degree of ionisation**, α, corresponding with the given dilution of the solution : $\Lambda_v/\Lambda_\infty = \alpha$. By the **dilution** is understood the reciprocal of concentration, *i.e.*, the number of c.c. containing 1 gm. equivalent of total electrolyte.

In practice, the concentration is usually measured in gm. equiv. per litre, and the dilution in litres per gm. equiv. In these units $\Lambda = (k/c') \times 1000$, or $(kv') \times 1000$.

The progressive ionisations of two typical electrolytes are seen from the tables below.

IONISATION OF KCl AT 18°.

c gm. equiv. per *litre*.	Equivalent conductivity $\Lambda = (k/c) \times 1000$	Degree of ionisation $\alpha = \Lambda/\Lambda_\infty$	Ionisation constant $K = \frac{\Lambda^2 c}{\Lambda_\infty - \Lambda}$
0	129·9	1·00	—
0·0001	129·1	0·994	0·0154
0·001	127·3	0·980	0·0485
0·01	122·4	0·943	0·1542
0·1	112·0	0·862	0·5405
1·0	98·3	0·757	2·350

IONISATION OF ACETIC ACID AT 18°

Dilution v *litres* per gm. equiv.	Equivalent conductivity $\Lambda = kv \times 1000$	Degree of ionisation $\alpha = \Lambda/\Lambda_\infty$	Ionisation constant K
0·334	0·6186	0·0016	$7{\cdot}7 \times 10^{-6}$
1·977	2·211	0·0057	$16{\cdot}5 \times 10^{-6}$
10·753	5·361	0·0138	$18{\cdot}0 \times 10^{-6}$
63·26	13·03	0·0336	$18{\cdot}5 \times 10^{-6}$
∞	387·9	1·0000	—

Potassium chloride is appreciably ionised even in normal solution: it is a typical **strong electrolyte**. Acetic acid is only slightly ionised, even in dilute solutions (when completely ionised it has a higher equivalent conductivity than potassium chloride, owing to the great mobility of the hydrogen-ion); it is a typical **weak electrolyte**. The significance of K will be considered later (p. 357).

Determination of conductivity.—If an ordinary current from a battery is passed between platinum electrodes in a solution of an electrolyte, and a galvanometer is included in the circuit, it will be found that the strength of the current diminishes as electrolysis proceeds. This diminution in current strength is partly due to the accumulation of the products of electrolysis at the electrodes. These form a galvanic cell which tends to send a current in the opposite direction to that driven round the circuit by the battery.

This reverse electromotive force, tending to oppose the direct electromotive force of the battery which is effecting decomposition, is known as the **electromotive force of polarisation.**

In order to obtain accurate measurements of the conductivity of electrolytes it is necessary to eliminate polarisation. F. W. Kohlrausch (1869) did this by using an **alternating current,** *i.e.*, a current which flows alternately in one direction and then in the other, with a very small interval of time between the reversals of direction. Such a current is supplied by an **induction coil** (without condenser) attached to a battery.

The ions are driven first in one direction and then in the other by the alternating current, and the amounts deposited on the electrodes are exceedingly small.

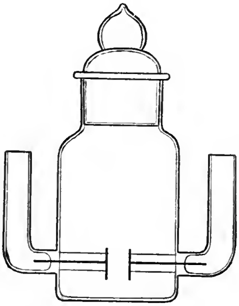


FIG. 161.—Cell for Measurement of Conductivity.

Polarisation is still further reduced by depositing platinum black on the electrodes, by electrolysing between them a solution of 1 gm. of chloroplatinic acid and 8 mgm. of lead acetate in 30 c.c. of water, with an accumulator, and reversing the current from time to time.

EXPT. 119.—A convenient type of **electrolytic cell** is shown in Fig. 161. It consists of a small stoppered bottle (shown full size), with parallel platinised platinum electrodes sealed in. The platinum wires from the electrodes, which are covered with glass inside the cell, pass into glass tubes on each side. A drop of mercury is poured into each tube, and the wires from the coil dip into the mercury to make contact. These wires then pass through rubber tubes, so that the cell, filled with a solution of KCl, say decinormal, and stoppered, may be immersed in a tank of water kept at a constant temperature, say 18° or 25°.

The alternating current is supplied by a small induction coil giving a high buzzing note, with one accumulator. Since a galvanometer cannot be used with an alternating current, a **telephone** is employed.

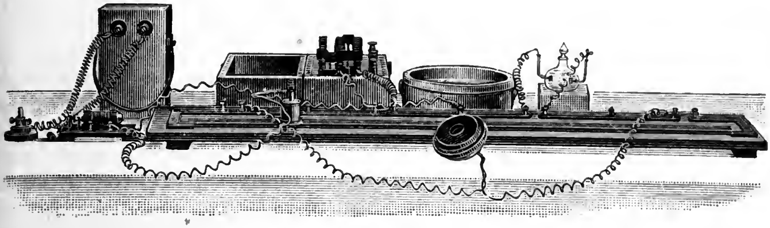


FIG. 162.—Apparatus for Measurement of Conductivity.

In order to measure the resistance, a resistance-box is connected with the conductivity cell, telephone, and coil, and a metre wire-bridge with a scale and sliding contact. Fig. 162 shows the apparatus set up for use. The connections are shown in Fig. 163.

The slider is placed near the middle of the bridge and plugs are taken out of the resistance box until the sound in the telephone is appreciably reduced. The slider is then moved about until the sound in the telephone is reduced to a minimum.

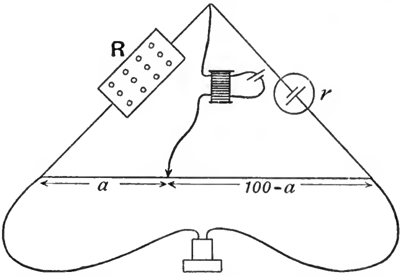


FIG. 163.—Diagram of Conductivity Apparatus.

Let a be the reading on the bridge, R the resistance taken out of the box: then the **resistance** of the conductivity cell, r, is, since the arrangement constitutes a Wheatstone bridge, given by $r = R \times \frac{a}{100 - a}$ ohms. The **conductance** is $1/r$, *i.e.*, the current passing, in amperes, for 1 volt potential difference between the electrodes. This follows from **Ohm's law**:

$$\text{Current in amperes} = \frac{\text{potential difference in volts}}{\text{resistance in ohms}},$$

which has been proved experimentally to apply to electrolytes.

The electrodes of the conductivity cell will not usually be exactly 1 sq. cm. in area, parallel, and 1 cm. apart, so that the conductance is not usually equal to the **conductivity** (p. 289). Since the relation between the two depends only on the construction of the cell, it is possible to determine once for all this ratio, called the **cell constant**, for a particular cell. This is done by using as electrolyte a solution of known conductivity: a normal solution of potassium chloride (74·55 gm. per litre), for which at 18° $k_{18^\circ} = 0{\cdot}09824$. If the resistance of the cell containing this solution is r ohms, $k_{18^\circ} = \frac{C}{r} = 0{\cdot}09824$, where C is the **cell constant.** If any other solution is now used, and if the resistance is r' ohms, the **conductivity** is $k'_{18^\circ} = C/r'$.

Neutralisation.—**Acids** are substances producing the **hydrogen-ion** in solution: $HCl \rightleftharpoons H^{\cdot} + Cl'$. **Bases** are substances producing the **hydroxide-ion** in solution: $NaOH \rightleftharpoons Na^{\cdot} + OH'$.

If an acid and a base in solution are mixed, a **salt** is formed, and the solution becomes neutral. This is usually represented by such equations as: $HCl + NaOH = NaCl + H_2O$. Since the acid, base, and salt are usually ionised in solution, the reaction really occurs between the ions: $(H^{\cdot} + Cl') + (Na^{\cdot} + OH') = (Na^{\cdot} + Cl') + H_2O$. It will be seen that the anion of the acid (Cl'), and the cation of the base ($Na^{\cdot}$), which together constitute the ions of the salt, take no part in the change: they are free before and after the reaction. The net change in **neutralisation** *is the union of the hydrogen-ion of the acid with the hydroxide-ion of the base to form practically undissociated water*: $H^{\cdot} + OH' = H_2O$.

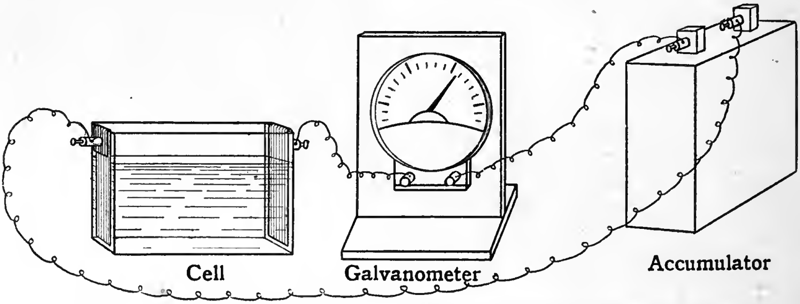


FIG. 164.—Apparatus to demonstrate Diminution in Conductivity on Neutralisation.

This is the sole reaction with strong acids and bases, *i.e.*, those which are practically completely ionised. Salts are nearly always largely ionised in solution.

The hydrogen- and hydroxyl-ions are those which possess the greatest mobility (p. 288). After neutralisation, therefore, when the rapid hydrogen- and hydroxyl-ions have been withdrawn, the conductivity of the solution will be appreciably diminished.

EXPT. 120.—Fit a rectangular glass trough with two electrodes of sheet copper (Fig. 164). Connect these through an ammeter with two accumulators in series. Pour into the cell a solution of N-caustic soda containing dissolved urea to increase its density, and coloured with phenolphthalein. Float a slice of cork on this solution and, by means of a pipette, introduce an equal volume of N-hydrochloric acid as a definite stratum above the alkali. Switch on the current and observe the deflection of the ammeter. This is a measure of the current carried by all the ions, $Na^{\cdot}$, $H^{\cdot}$, OH', Cl'. Now stir the two liquids with a glass rod, and notice the reduced reading of the ammeter. The ions $Na^{\cdot}$ and Cl' alone now carry the current.

A modification of this method may be used in **titrating** an alkaline or acid solution which is too strongly coloured to allow of an indicator being used.

Heat of neutralisation.—If the theory of neutralisation given above is true, the heat evolved in the neutralisation of one equivalent of a strong base by one equivalent of a strong acid should be the same for different acids and bases, since the reaction in all cases is the same, viz., the union of hydrogen-ions from the acid with hydroxide-ions from the base to form practically undissociated water.

This unexpected result has been verified by experiment; the heat of neutralisation is, per equivalent of strong acid and base, equal to about 13·7 kgm. cal.

$HCl\,Aq + NaOH\,Aq$ 13·70	$HNO_3\,Aq + NaOH\,Aq$ 13·70
$HBr\,Aq + KOH\,Aq$ 13·76	$HCl\,Aq + \frac{1}{2}Ba(OH)_2\,Aq$ 13·80.

If the acid or the base is weak, heat will be evolved or absorbed during the neutralisation, since the un-ionised acid or base will dissociate as neutralisation proceeds, and hydrogen-ions and hydroxide-ions are removed; this dissociation will, in general, be attended by an absorption or evolution of heat. An example of this behaviour is the neutralisation of hydrofluoric acid (p. 421). If the salt formed is only slightly ionised (a case which is very rare), or is insoluble, the heat of neutralisation will also be abnormal, since the association of the ions of the salt to form undissociated molecules, or the precipitation of the salt, are processes attended by heat changes.

Ionisation in stages.—Molecules which are capable of giving more than two ions on dissociation often dissociate in stages. This is not always the case. Thus, potassium ferrocyanide, $K_4Fe(CN)_6$, ionises directly according to the equation: $K_4Fe(CN)_6 = 4K^{\cdot} + Fe(CN)_6''''$, whilst sulphuric acid ionises in two stages: $H_2SO_4 = H^{\cdot} + HSO_4'$, followed by $HSO_4' = H^{\cdot} + SO_4''$. The second stage of the dissociation occurs only to a very limited extent, except in very dilute solutions.

At moderate dilutions, therefore, sulphuric acid should behave as a monobasic acid. The conductivity shows that this is the case. But if the acid is neutralised with caustic soda, the hydrogen-ion is completely eliminated, with the hydroxide-ion of the base, in the form of water: $H_2SO_4 + 2Na^{\cdot} + 2OH' = 2Na^{\cdot} + SO_4'' + 2H_2O$.

The reason for this behaviour is the ionisation of the HSO_4' ion into $H^{\cdot}$ and SO_4''. As soon as the hydrogen-ion corresponding with the first stage of the ionisation: $H_2SO_4 = H^{\cdot} + HSO_4'$, has been removed, the HSO_4' ion begins to dissociate to a slight extent. The trace of hydrogen-ion so produced, however, is at once removed by the hydroxide-ion of the base added, and further ionisation of HSO_4' results. This goes on until all the HSO_4' has been ionised, and finally only SO_4'' ions remain. This, however, corresponds with the formation of the normal salt, and the acid, therefore, behaves as if it were dibasic.

Manufacture of chlorine and alkali by electrolysis.—The electrolysis of brine, *i.e.*, a solution of sodium chloride, studied in Expt. 116, is applied on a large scale for the manufacture of caustic soda and chlorine.

The **Castner-Kellner cell** consists (Fig. 165) of a shallow slate tank divided into three compartments by slate partitions not quite touching the floor. The floor is covered by a pool of mercury, thus separating the three compartments. Each end compartment is filled with strong brine, the middle one with water. Anodes of carbon, as shown, or of platinum gauze, are placed in the end compartments, whilst the cathode consists of a bundle of iron rods in the central compartment. Chlorine is evolved in the end compartments, and is led off by earthenware pipes. Sodium ions are discharged on the mercury in the end compartments, and the sodium dissolves in the mercury, forming sodium amalgam. The cell is given a slow rocking motion by an eccentric, and the sodium amalgam is brought from the end compartments to the middle compartment, where it decomposes the water, forming a solution of caustic soda. Hydrogen is evolved from the iron cathode. In the new type of cell the tank is stationary, and the mercury is moved by an archimedean screw, finally dropping over a cascade into water to free it from sodium, after which it re-enters the cell. The Castner-Kellner cell is used at Niagara; a smaller plant is in operation at Weston Point, near Liverpool.

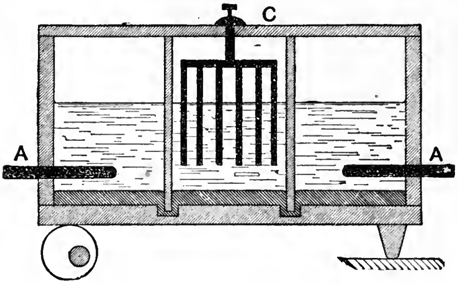


FIG. 165.—Castner-Kellner Cell.

The Electro-Bleach Company, at Middlewich, in Cheshire, use the **Hargreaves-Bird cell.** The cell consists of a narrow rectangular box (Fig. 166), the top and bottom of which are of cast iron, and the sides of asbestos-board soaked in sodium silicate to act as diaphragms. Outside the diaphragms, and in contact with them, are the cathodes of copper gauze. The anodes are inside the chamber, and consist of five lead cores, on which are strung rough blocks of gas-carbon, the exposed lead being covered with cement. Brine is fed in at the bottom of the cell, and the spent liquor, still containing about one-third of the salt undecomposed, runs off to waste from the top. The sodium ions pass through the diaphragms, and are discharged on the cathodes. Steam is blown on to these, which are enclosed in an outer iron casing, and a solution of caustic soda obtained. Chlorine escapes from a pipe at the top of the anode chamber. The gas may be diluted with air, and used in the manufacture of bleaching powder, or liquefied by compression to 6 atm. at 15°, or by cooling at ordinary pressure in iron pipes. It is sent out as liquid chlorine in steel cylinders. The electrolytic chlorine is purer and more concentrated than that made by chemical methods. Some of it is used in making stannic chloride, or chlorinated acetylenes (p. 680).

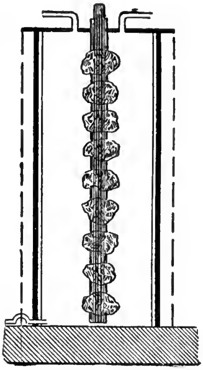


FIG. 166.—Hargreaves-Bird Cell.

SUMMARY OF CHAPTER XVI

Faraday's Laws of Electrolysis: (1) The weight of an ion deposited in a given time is proportional to the strength of the current ; (2) 96,000 coulombs liberate 1 gm. equiv. of any ion. This quantity of electricity, 96,000 cmb., is called a **faraday**, denoted by **F.**

Theory of Electrolytic Dissociation : Salts in solution are dissociated into electrically-charged atoms or radicals, called **ions.** These ions carry the current in electrolysis. The charge on an ion is either positive (cation), or negative (anion), and is always equal to the fundamental charge, ϵ, multiplied by the valency of the ion. The unit charge, ϵ, is identical with the charge of the atom of free negative electricity, or the **electron.** Its value is $1{\cdot}59 \times 10^{-19}$ cmb. Free positive electricity is not known ; a positive ion is an atom or radical which has lost one or more negative electrons. The **conductivity** of an electrolyte is the current in amperes which passes through the solution contained in a cubical cell with sides 1 cm. long when the opposite sides, forming electrodes, are connected with a potential difference of 1 volt. The **equivalent conductivity** of a solution is the conductivity divided by the concentration in gm. equiv. per c.c. : $\Lambda = k/c$. It increases with dilution, since the ionisation increases. The **degree of ionisation** measured by the ratio of the equiv. conduct. at a given concentration to the equiv. conduct. at infinite dilution, corresponding with complete ionisation, $\alpha = \Lambda_v/\Lambda_\infty$.

Neutralisation of a strong acid by a strong base is the union of the hydrogen-ion of the acid with the hydroxide-ion of the base to form undissociated water. The ionisation of water is very small.

EXERCISES ON CHAPTER XVI

1. Describe what happens when an electric current is passed between platinum plates through solutions of (*a*) copper sulphate, (*b*) sodium sulphate, (*c*) potassium chloride. Distinguish between primary and secondary products of electrolysis.

2. How is caustic soda manufactured by electrolysis from common salt? In order to decompose 1 kgm. of salt, how many ampere-hours (1 ampere flowing for 1 hour) are theoretically necessary?

3. State Faraday's Laws of Electrolysis. What experiments would you make in order to demonstrate the truth of these laws?

4. Give a short account of the theory of electrolytic dissociation, and indicate what explanations it gives of (*a*) electrolysis, (*b*) the heat of neutralisation of a strong acid by a strong base.

5. Represent by ionic equations the following reactions: (*a*) the solution of magnesium in hydrochloric acid, (*b*) the action of water on sodium, (*c*) the preparation of chlorine from manganese dioxide and hydrochloric acid, (*d*) the precipitation of silver nitrate solution by a solution of sodium chloride.

6. What are electrons ? How has the absolute value of the charge of an electron been determined ? From this, how is it possible to calculate the number of molecules of hydrogen in 1 c.c. of hydrogen gas at S.T.P. ?

7. What weight of silver is deposited from a solution of silver nitrate by a current of 0·075 ampere flowing for seventeen minutes ?

8. Describe how the speed of migration of an ion may be measured. How does it compare with the speed of diffusion of a gas, and what connection is there between the two?

9. What is the degree of ionisation of an electrolyte ? How may it be measured, and how does it change with dilution ?

10. A current of 0·1 amp. is passed for forty-five minutes through a voltameter containing acidulated water, and one containing copper sulphate solution with copper electrodes. What volume of electrolytic gas (at S.T.P.) will be evolved, and what weight of copper deposited ?

CHAPTER XVII

THE MOLECULAR WEIGHTS OF SUBSTANCES IN SOLUTION

The molecular depression of freezing point.—The lowering of the freezing point of a solvent by a substance in solution is proportional to the concentration of the latter (p. 103). Thus, with cane-sugar in water:

Gm. of sugar in 100 grams of water = C.	Freezing point lowering = D.	Ratio D/C.
11·4	0·62°	0·0544
22·8	1·23°	0·0544
34·2	1·85°	0·0544

The depression of freezing point produced by 1 gm. of sugar in 100 gm. of water is 0·0544°; that by n gm. is 0·0544n°. The depression produced by 1 gm. of another substance will be different, *e.g.*, 1 gm. of urea lowers the freezing point of 100 gm. of water by 0·31°.

Raoult (1883) made the important discovery that **if quantities proportional to the molecular weights of different substances are dissolved in identical weights of a solvent, the freezing points of all the solutions are the same.** A molecular weight in grams of a substance dissolved in 1 kilogram of water depresses the freezing point of the latter by 1·85°. This is called the **molecular depression of freezing point,** Δ, for water.

Thus, if 342 gm. of cane-sugar, corresponding with the formula $C_{12}H_{22}O_{11}$, are dissolved in 1 litre of water, the solution freezes at −1·852°. The same freezing point is shown by solutions of 60 gm. of urea, CON_2H_4, or 46 gm. of alcohol, C_2H_6O, in 1 litre of water, since these are equi-molecular amounts.

The molecular depression varies with the solvent. Thus, if 46 gm. of absolute alcohol are dissolved in 1 kilogram of benzene,

C_6H_6, the solution freezes at 0·5°. The freezing point of pure benzene is 5·4°, hence the molecular depression of freezing point for that solvent is 4·9°. The values of the molecular depressions for some common solvents are as follows :

	Δ	M. pt.		Δ	M. pt.
Water	1·862°	0°	Formic acid	2·8°	8°
Acetic acid	3·9°	17°	Phenol	7·27°	40°
Benzene	4·9°	5°			

Van't Hoff (1886) showed that Δ may be calculated from the **latent heat of fusion,** L_f, and the **absolute melting point,** T_f, of the solvent, by the formula : $\Delta = \frac{0{\cdot}002\,T^2}{L_f}$. For water : $L_f = 79{\cdot}77$, $T_f = 273$, $\therefore \Delta = 0{\cdot}002 \times (273)^2/79{\cdot}8 = 1{\cdot}869$.

It is clear that a measurement of the freezing point of a solution enables us to find the **molecular weight of the dissolved substance,** in the state in which it exists in solution.

Let the depression of freezing point produced by m gm. of solute per kgm. of solvent be D. That produced by the molecular weight, M, in 1 kgm. we know is the molecular depression **Δ.** Further, we know from Blagden's law that the two depressions are proportional to the two concentrations :

$$\therefore \quad m : M :: D : \Delta$$

$$\text{hence} \quad M = m \times \frac{\Delta}{D}.$$

Example.—1·35 gm. of carbon tetrachloride were dissolved in 55 gm. of acetic acid. The freezing point of the latter was depressed from 16·750° to 16·132°. Find the molecular weight of carbon tetrachloride.

m = No. of gm. of solute per 1000 gm. of solvent = 1·35 × 1000/55
Observed depression = 16·750 − 16·132 = 0·618° = D.
Molecular depression for acetic acid = 3·9° = Δ.
Molecular weight of solute $M = \frac{m\,\Delta}{D} = \frac{1{\cdot}35 \times 1000 \times 3{\cdot}9}{55 \times 0{\cdot}618} = \mathbf{155}$.

The molecular weight calculated from the vapour density is CCl_4 = **153,** hence we conclude that carbon tetrachloride has the same molecular weight in the state of vapour as in solution in acetic acid ; in both cases the formula is CCl_4.

Raoult's law holds good only if the solution is **dilute** ; apparent exceptions are also shown by aqueous solutions of acids, bases, and salts (*i.e.*, **electrolytes**) ; these correspond with the **ionisation** of the substances. In its application to the determination of molecular weights, two conditions must therefore be satisfied : (i) *the solution must be dilute,* and (ii) *the solution must not be an electrolyte.*

Determination of molecular weights by the freezing-point method.—The **apparatus** used in the determination of molecular weights from the depression of freezing point is shown in Fig. 167. A very sensitive thermometer, called a **Beckmann thermometer**, *D*, is used, which has only six degrees on the whole scale, the latter being graduated in thousandths of a degree. There is a reservoir at the top of the capillary tube, into which mercury can be shaken if higher temperatures are used (*e.g.*, phenol, m. pt. 40°), or from which mercury can be drawn into the tube and bulb if lower temperatures (*e.g.*, water, 0°) are to be used. It is of no consequence what the actual readings on the scale are, it is only their *difference*, *D*, which is required. The solvent is weighed into the tube *A*, and a stirrer of bent platinum wire introduced. The thermometer is now fitted into the tube through a cork, so that the bulb is covered with the liquid.

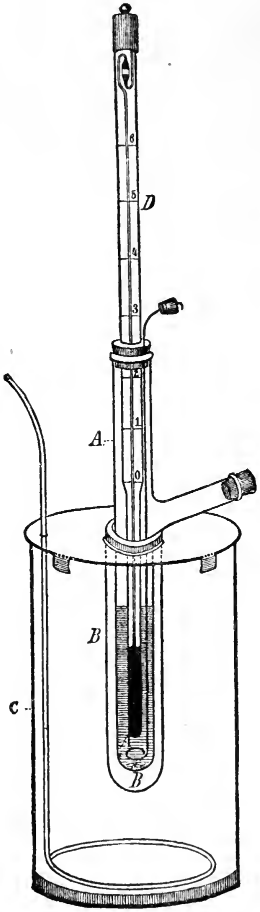


FIG. 167.—Beckmann's Freezing-point Apparatus.

The tube *A* is then fitted through a cork into a large test-tube, *B*, which serves as an air-jacket, and prevents the fall in temperature being too rapid. The tube *B* is plunged into a freezing mixture (*e.g.*, ice and salt) contained in the large jar, *C*. The stirrers in the solvent tube and outer jar are worked up and down, and the thermometer observed. The mercury falls steadily to a certain point, when the solvent is slightly supercooled. Freezing then commences, the temperature at once runs up to the freezing point, and afterwards remains stationary. It is then read off with a lens, the thermometer being gently tapped to prevent any adhesion of the mercury to the glass. Suppose the reading is 3·216°.

The tube *A* is then taken out, and allowed to warm until the solvent liquefies. A weighed quantity of the substance under investigation is introduced through the side tube, and dissolved by working the stirrer. The tube is replaced in the air-jacket, and the latter again put into the freezing mixture. The process is carried out further exactly as with the pure solvent, and the freezing point read off. Suppose this to be 2·839°; then D, the **depression of freezing point**, is $3{\cdot}216 - 2{\cdot}839 = 0{\cdot}377°$.

A mixture of ice and salt is used in the outer jar if the solvent is water; ice and water are used for benzene, acetic acid, and formic acid; phenol is melted in warm water, and the inner tube and air-jacket are supported in a clamp without outer jar. Acetic and formic acids, and phenol, readily absorb moisture, which lowers their freezing points. Care must be taken to prevent this occurring during the experiment.

EXAMPLE.—17·79 gm. of an aqueous solution containing 0·1834 gm. of hydrogen peroxide froze at $-0{\cdot}571°$. What is the molecular weight of hydrogen peroxide in the solution?

0·1834 gm. of hydrogen peroxide is dissolved in $17{\cdot}79 - 0{\cdot}183 = 17{\cdot}607$ gm. of water

$$\therefore \text{wt. of peroxide in 1 kgm. of water} = \frac{0{\cdot}1834 \times 1000}{17{\cdot}607} = 10{\cdot}42 \text{ gm.} = m.$$

Let M = mol. wt. of hydrogen peroxide, then:

$$10{\cdot}42 : M = 0{\cdot}571 : 1{\cdot}86$$

$$\therefore M = 10{\cdot}42 \times \frac{1{\cdot}86}{0{\cdot}571} = \mathbf{33{\cdot}9}.$$

The formula H_2O_2 gives $M = 34$.

Vapour pressures of solutions.—It has already been mentioned (p. 104) that salt, when dissolved in water, lowers the vapour pressure of the latter. This is quite general: if a non-volatile substance is dissolved in a volatile solvent, the vapour pressure of the solution is lower, at a given temperature, than that of the pure solvent. Further, if f_0 is the vapour pressure of the pure solvent, f that of the solution, the ratio $\left(\frac{f_0 - f}{f_0}\right)$, or the **relative lowering of vapour pressure,** is found to be (1) proportional to the concentration of the solution; (2) practically independent of temperature within certain limits; (3) the same for equimolecular amounts of different substances in the same weight of a solvent. (Raoult, 1887.)

The **molecular lowering of vapour pressure** is therefore a constant for a given solvent. In a solution containing N_0 gm. mol. of solvent and N gm. mol. of solute, the relative lowering of vapour pressure is found by experiment to be given by the equation:

$$(f_0 - f)/f_0 = N/(N_0 + N).$$

Thus, if 1 gm. mol. of solute is dissolved in 99 gm. mol. of solvent, there will be a lowering of vapour pressure of 1 per cent., since $N/(N_0 + N) = 1/(99 + 1) = 0{\cdot}01$. The value of N_0 is calculated from the weight of solvent taken divided by its molecular weight in the state of *vapour*, *i.e.*, N_0 is the number of **vapour molecules.**

EXAMPLE.—Pure benzene, C_6H_6, has a vapour pressure of 751·86 mm. at 80°. When 2·47 gm. of ethyl benzoate are dissolved in 100 gm. of benzene, the solution has a vapour pressure of 742·6 mm. The molecular weight of benzene vapour is 78 $\therefore$ $N_0 = 100/78 = 1{\cdot}283$. Also $(f_0 - f)/f_0 = (751{\cdot}86 - 742{\cdot}6)/751{\cdot}86 = 0{\cdot}0123$ $\therefore$ $0{\cdot}0123 = N/(1{\cdot}283 + N)$ $\therefore$ $N = 0{\cdot}01598$. But $N = 2{\cdot}47/$(mol. wt. of ethyl benzoate) $\therefore$ mol. wt. of dissolved ethyl benzoate $= 2{\cdot}47/0{\cdot}01598$ $=$ **154·6.** That calculated from the vapour density, or the formula $C_6H_5{\cdot}COO{\cdot}C_2H_5$, is 150.

Boiling points of solutions.—Lowering of vapour pressure is synonymous with **elevation of boiling point**, since the latter is the temperature at which the vapour pressure reaches atmospheric pressure, or 760 mm. The boiling point of water is 100°, because at 100° the vapour pressure of pure water is 760 mm. If salt is dissolved in the water, the vapour pressure at 100° is less than 760 mm., and it will be necessary to raise the temperature above 100° to attain that pressure, *i.e.*, the boiling point of the water is raised by the dissolved substance. Let *AA* (Fig. 168) be the vapour pressure curve of the pure solvent, *BB* that of the solution. Since the relative lowering of vapour pressure for a given concentration is independent of temperature between certain limits, the curve *BB* will be at a constant distance from the curve *AA*. If we draw a horizontal line through $p = 760$ mm. it cuts the curves at points corresponding with the boiling point of the pure solvent, and that of the solution, respectively, viz., t_0, t_1. If we have a still more concentrated solution, the vapour pressure curve of which is *CC*, the boiling point is t_2, and $t_2 > t_1 > t_0$. The vapour pressures at the temperature t_0 are t_0a, t_0b, t_0c, respectively. If c_1, c_2 are the concentrations of the two solutions, the lowerings *ab*, *ac* are proportional to c_1, c_2 (since f_0 is constant). But, since the curves are parallel, $ab : ac :: ae : ah$, *i.e.*, the elevation of boiling point is proportional to the lowering of vapour pressure, and both are proportional to the concentration :

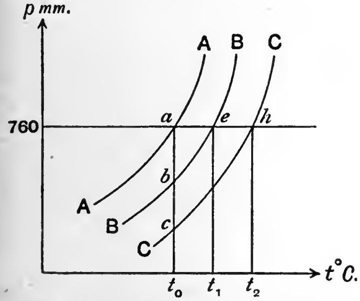


FIG. 168.—Vapour Pressure Curves of Solutions.

$$\delta p_1 : \delta p_2 :: \delta t_1 : \delta t_2 :: c_1 : c_2.$$

The elevation of boiling point of a solution is often applied in the laboratory to produce a heating-bath of higher temperature than 100°. For this purpose, solutions of the very soluble salt calcium chloride are convenient. They may be boiled in iron vessels. The boiling points for given amounts of anhydrous salt are as follows:

Parts of calcium chloride per 100 parts of water:	50	200	325
Boiling point:	112°	158°	180°

Such high-temperature baths may replace those using oil, glycerin, or fusible metal, except at temperatures above 200°.

It follows that the **molecular elevation of boiling point** is constant for a given solvent. It is taken as the rise in boiling point for 1 gm. mol. of non-volatile solute in 1 kgm. of solvent; we may denote it by E.

If w gm. of substance in 1000 gm. of solvent raise the boiling point $D°$, we shall have the proportion $D : E :: w : M$, where M is the molecular weight of the dissolved substance. Hence $M = \frac{Ew}{D}$ (*cf.* the freezing-point equation: $M = \triangle w/D$, p. 300).

The values of E for a few solvents are given below.

Solvent.	Boiling point °C.	Molecular elevation of Boiling point, E.
Water	100	0·52
Chloroform	61·2	3·66
Methyl alcohol	64·7	0·88
Ethyl alcohol	78·3	1·15
Ether	35·4	2·10
Benzene	80·2	2·57

The value of E may be calculated from the **latent heat of evaporation** of the solvent, L_e, in a similar way to that of Δ from the latent heat of fusion. If T is the absolute boiling point,

$$E = \frac{0{\cdot}002\,T^2}{L_e}.$$

Thus, for **water**: $T = 100 + 273 = 373$; $L_e = 538$

$$\therefore E = 0{\cdot}002 \times (373)^2 \div 538 = 0{\cdot}517 \text{ (obs. } 0{\cdot}52).$$

The above equation does not hold for concentrated solutions, or for solutions of electrolytes (p. 300). It applies to many organic substances (*e.g.*, sugar, urea) in water, and in organic solvents.

Example.—The molecular weight of **iodine** dissolved in ether may be calculated from the following figures:

2·0579 gm. of iodine dissolved in 30·14 gm. of ether gave an elevation of boiling point of 0·566°.

$w = 2{\cdot}0579 \times 1000/30{\cdot}14 = 68{\cdot}28$; $D = 0{\cdot}566°$; $E = 2{\cdot}10°$

$\therefore M = Ew/D = 2{\cdot}10 \times 68{\cdot}28/0{\cdot}566 = \mathbf{253{\cdot}3}$. But $I_2 = 2 \times 126 = 252$, $\therefore$ iodine exists as diatomic molecules, I_2, in solution in ether.

Determination of the elevation of boiling point.—The apparatus for the determination of the molecular weight of a dissolved substance from the elevation of the boiling point of a solvent, devised by Beckmann, is shown in Fig. 169. The thermometer and the tube for holding the solution are the same as those used in the freezing-point apparatus (p. 301), except that the tube has a short piece of platinum wire sealed through the bottom to assist in the transmission of heat, and contains a layer of small crystals of garnet to prevent bumping. The tube is surrounded by a glass mantle, plugged with asbestos, and the closed end of the tube, with the platinum wire projecting, is heated over a slightly smaller hole in a piece of asbestos millboard, with wire-gauze beneath, by means of a small Bunsen flame, so as to get a uniform temperature. The vapour of the solvent formed in the tube is condensed in a reflux condenser, most conveniently formed of a limb of the tube, as shown, and the liquid flows back. The boiling point of the pure solvent is first found in terms of an arbitrary reading on the Beckmann thermometer, the mercury column in the latter having been suitably adjusted. A weighed quantity of solvent is used for this purpose. The tube is then cooled, and a weighed quantity of the substance, the molecular weight of which is to be found, is introduced through the side tube and completely dissolved. The boiling point of the solution is then found. The difference is *D*, the elevation of boiling point.

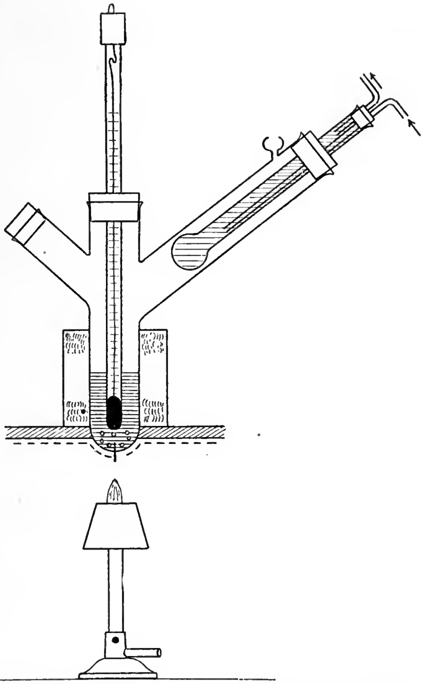


FIG. 169.—Beckmann's Apparatus for Determination of Elevation of Boiling Point.

A more convenient apparatus is that of Landsberger, modified by Beckmann (1902), in which the solution is heated by passing through it the vapour of the solvent. The latter condenses, giving out heat and raises the temperature of the solution (which is, of course, becoming diluted), until the boiling point is reached. The vapour of the solvent then passes through without condensation. The glass tube *A* (Fig. 170) contains the solvent, and is heated in the same way as in the preceding apparatus. Inside is the tube *B*, graduated in mm., containing the solution and the thermometer. Vapour from *A* bubbles through the solution by way of the tube *C*, open to the vapour in *A*. The tube *R* prevents liquid from *B* being sucked back into *A*. The vapour is condensed in *E*, and the liquid can be allowed to flow back into *B*, or, by turning the condenser in the ground joint, returned to *A* through the siphon-tube *F*, the opening of which is brought opposite a hole shown. The concentration of the solution when vapour passes freely through it and the boiling point remains constant is determined by weighing.

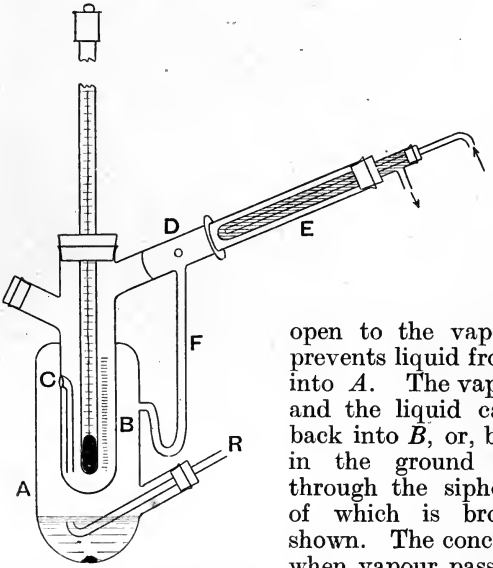


FIG. 170.—Landsberger Boiling-point Apparatus—Beckmann.

Deliquescence.—If a beaker containing pure water and one containing a solution of a salt, or other non-volatile substance, in water are placed side by side under an evacuated receiver (Fig. 171), each liquid emits aqueous vapour into the space above. If the vapour pressures were the same, equilibrium would be established with a definite pressure of vapour in the space—this, in fact, occurs when either liquid is separately confined under the receiver. In this state as many molecules of water are leaving the liquid per second by evaporation as are returning to it by condensation. But the vapour pressure of the pure water is always higher than that of the solution, hence the pure water tends to saturate the space with vapour under a higher pressure than can remain in equilibrium with the solution. Condensation of vapour occurs on the latter, and the pure water is gradually transferred completely to the solution by this

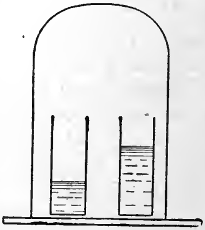


FIG. 171.—Isothermal Distillation.

process of **isothermal distillation**, the solution becoming diluted. Equilibrium is set up when all the pure water is evaporated and absorbed by the solution, and a little aqueous vapour exists in the space under a pressure equal to the vapour pressure of the diluted solution.

Many solid salts, such as potassium carbonate and calcium chloride, become damp on exposure to moist air, and in time liquefy completely. This liquefaction of solids on exposure to moist air is called **deliquescence**. All deliquescent substances are very soluble in water, and this suggests the explanation of the change. If a trace of moisture is present in the solid, a little saturated solution is formed. Since this is very concentrated, its vapour pressure can be less than the partial pressure of aqueous vapour in the atmosphere, however low the latter may be. Moisture is attracted by the salt, which gradually liquefies completely to a saturated solution. The latter then goes on absorbing aqueous vapour until its dilution is such that the vapour pressure is equal to the partial pressure of water vapour in the air.

Solid substances which attract moisture without liquefaction, such as recently-ignited charcoal, and liquids such as alcohol and sulphuric acid which absorb moisture, are called **hygroscopic.** In the first case the moisture appears to be condensed on the surface of the charcoal by molecular attraction (*cf.* p. 270). A similar cause may explain the *commencement* of the deliquescence of recently-fused calcium chloride, caustic potash, etc.

Osmotic pressure.—If a concentrated solution of copper sulphate, contained in the lower part of a cylinder, is covered with a layer of water, the copper sulphate molecules gradually **diffuse** upwards until the solution becomes homogeneous, and of uniform colour (p. 258). The dissolved molecules thus behave to some extent like those of a gas; in both cases they are in motion, *i.e.*, they possess **kinetic energy.** If we could interpose a partition in the solution, with pure water above, which would stop the dissolved copper sulphate molecules from passing, but would be freely permeable to water, we should expect the copper sulphate molecules to exert a bombardment **pressure** on the partition. A partition which is freely permeable to pure solvent, but is impermeable to dissolved substances, is called a **semipermeable partition,** or—since it is usually prepared in the form of a thin film—a **semipermeable membrane.**

A semipermeable membrane may be regarded as a kind of **molecular sieve,** or **filter.** Just as an ordinary filter-paper will stop suspended particles, and permit dissolved molecules to pass through, the semipermeable membrane may be regarded as stopping even the dissolved molecules, and permitting only the molecules of pure solvent to pass through. There is, however, a difference between the two cases: in order to squeeze pure solvent through the semipermeable membrane it is necessary to apply a definite, and often large, **pressure** to the solution enclosed in it. At lower pressures no solvent percolates through the partition.

Various substances have been discovered which function as semipermeable membranes. Without exception they are slimy, non-crystalline bodies, called **colloids** (p. 314). Thus, if a drop of copper sulphate solution is introduced into a solution of potassium ferrocyanide from a pipette, a skin or pellicle forms over it, composed of **copper ferrocyanide**, $Cu_2FeC_6N_6$. This substance is produced as a reddish-brown, gelatinous precipitate when the two solutions are mixed: $2CuSO_4 + K_4FeC_6N_6 = Cu_2FeC_6N_6 + 2K_2SO_4$. The pellicle is semipermeable, because if we allow the drop to stand in the solution, no copper salt diffuses through, as may be seen from the ferrocyanide solution remaining clear. The drop usually, however, expands or shrinks, owing to passage of *water* in or out through the pellicle. By holding the drop suspended, with a bright light behind the beaker, the streaks due to changes of concentration may be seen.

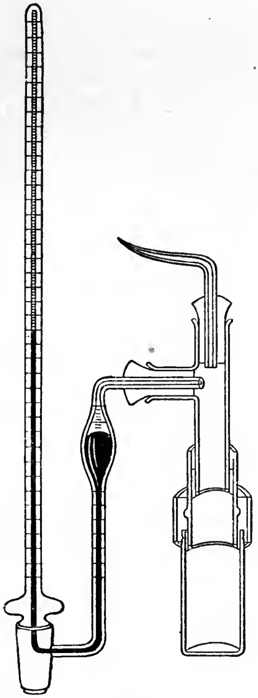


FIG. 172.—Pfeffer's Apparatus for Measurement of Osmotic Pressures.

EXPT. 121.—Into a strong solution of sodium silicate place small pieces of ferric chloride, nickel chloride, cobalt chloride, and copper chloride. Observe the formation of pellicles, which assume curious shapes on standing. ("**Chemical Garden.**")

Measurement of osmotic pressure.—In order to give strength to the membrane, so as to make it capable of withstanding considerable pressures, Pfeffer in 1877 deposited the copper ferrocyanide in the walls of an unglazed earthenware cell, such as is used for the porous pots in galvanic batteries.

The pot is immersed in copper sulphate solution, and placed under the receiver of an air-pump. The air in the pores is then removed, and on admitting air to the receiver, the copper solution is forced into the pores of the pot. The latter is removed from the solution, quickly washed out, and filled up with a 3 per cent. solution of potassium ferrocyanide. The pot is then allowed to stand for several hours in copper sulphate solution. The two salts diffuse through the porous wall, meeting somewhere inside, and producing a coherent film of copper ferrocyanide in the wall of the pot. The latter is now washed out, filled up with a solution, say of sugar in water, and fitted with a manometer cemented into the open top as shown in Fig. 172. When the pot is plunged into water, there is a gradual rise of pressure in the manometer, until a steady value is finally reached. This is called the **osmotic pressure** of the solution.

The preparation of a good semipermeable pot is a matter of no little difficulty; most of the results are failures, and many precautions must be taken which cannot be described here. Better results are obtained by driving the ions, $Cu^{\cdot\cdot}$ and $FeCy_6''''$, by electrolysis into the pot.

The laws of osmotic pressure.—The osmotic pressures of solutions of moderate concentrations are very considerable, as will be seen from the results on page 310 of Morse and Frazer (1905-1913) for cane-sugar. The concentrations are in gm. mol. ($C_{12}H_{22}O_{11} = 342$) per kgm. of water.

From these figures some important results are easily deduced. We shall at first consider **dilute solutions**, less than 0·5 molar (*i.e.*, less than 0·5 gm. mol. per litre).

If we divide the pressures at 0° by the concentrations (omitting the anomalous figure for 0·1 molar) we find :

Concentration, C =	0·2	0·3	0·4	0·5 gm. mol./kgm. H_2O.
Pressure, P =	4·722	7·085	9·442	11·895 atm.
Ratio P/C =	23·6	23·6	23·6	23·8.

The ratio is practically constant, hence **the osmotic pressure, at a constant temperature, is proportional to the concentration.** This is the exact analogue of **Boyle's law** for gaseous pressures.

If we next consider the osmotic pressures at various teperatures, taken on the absolute scale, for a fixed concentration, we find, for 0·2 molar :

Abs. temp., T	273	278	283	288	293	298°	
Pressure, P	4·772	4·818	4·893	4·985	5·064	5·148	atm.
Ratio P/T	0·0175	0·0173	0·0173	0·0173	0·0173	0·0173	

The ratio is constant, hence **the osmotic pressure, for a given concentration, is proportional to the absolute temperature.** This is the exact analogue of **Gay-Lussac's law** for gaseous pressures.

Concentration.		Temperature.					
		0°	5°	10°	15°	20°	25°
0·1	Mean Osmotic Pressure in Atmospheres.	(2·462)	2·452	2·498	2·541	2·590	2·634
0·2		4·722	4·818	4·893	4·985	5·064	5·148
0·3		7·085	7·198	7·334	7·476	7·605	7·729
0·4		9·442	9·608	9·790	9·949	10·137	10·296
0·5		11·895	12·100	12·297	12·549	12·748	12·943
0·6		14·381	14·605	14·855	15·144	15·388	15·624
0·7		16·886	17·206	17·503	17·815	18·128	18·434
0·8		19·476	19·822	20·161	20·535	20·905	21·252
0·9		22·118	22·478	22·884	23·305	23·717	24·126
1·0		24·825	25·283	25·693	26·189	26·638	27·053

Concentration.		Temperature.					
		30°	40°	50°	60°	70°	80°
0·1	Mean Osmotic Pressure in Atmospheres.	2·474	2·560	2·635	2·717	—	—
0·2		5·044	5·163	5·278	5·437	—	—
0·3		7·647	7·844	7·974	8·140	—	—
0·4		10·295	10·599	10·724	10·866	—	—
0·5		12·978	13·355	13·504	13·666	13·991	—
0·6		15·713	16·146	16·319	16·535	16·820	—
0·7		18·499	18·932	19·202	19·404	19·568	—
0·8		21·375	21·803	22·116	22·327	22·567	23·062
0·9		24·226	24·735	25·123	25·266	25·562	25·919
1·0		27·223	27·701	28·213	28·367	28·624	28·818

Thus, dilute solutions obey the two gas laws when "osmotic pressure" is substituted for "gas pressure." A much more striking result may, however, still be brought to light. If 1 gm. mol. of an ideal gas is confined in a space of 22·24 litres at 0° it will exert a pressure of 1 atm. Boyle's law then shows that if the volume is now reduced to 1 litre, the resulting pressure will be 22·2 atm. The gas has then unit concentration. The ratio P/C in the table, *i.e.*, the pressure for unit concentration, is, however, practically constant, and equal to 23·6. This is, within a few per cent., equal to 22·2, hence **the osmotic pressure of a solution is equal to the gas pressure which the solute would exert if all the solvent were removed, and the dissolved substance were left in the space in the condition of an ideal gas.** Solutions therefore obey **Avogadro's law.**

Van't Hoff, to whom these results are due (on the basis of the older and less accurate experiments of Pfeffer), summarised them in the statement that **dissolved substances obey the gas laws.** This is known as **Van't Hoff's gaseous theory of solution**; more accurate experiments, such as those quoted above, show that it is only approximately true, but it is probable that the laws are exact only in the limiting case of extreme dilution, just as the gas laws are exact only at infinitely small pressures. The gaseous theory of solution is the basis of modern physical chemistry; its consequences have had a most remarkable influence on the progress of the whole science during the last thirty years. The accumulated evidence leaves no vestige of doubt as to its truth as a broad generalisation, and the deduction of the laws of dilute solutions from thermodynamics strengthens this conclusion.

The Brownian movement.—An obvious step from the gaseous theory of solution is to identify osmotic pressure with **molecular bombardment** by the dissolved substance. Boltzmann was able to show, on the assumption that the solute molecules had the same mean kinetic energy as gas molecules, that the laws of osmotic pressure followed from the kinetic theory. This would imply that the molecular pressure pre-existed in the solution before the latter is separated from the solvent by the semipermeable wall, and that the function of the latter is merely to make the pressure evident. The idea met with great opposition, and gradually dropped out of sight, until it was revived, and put on the basis of an experimental fact, by the fascinating researches of Jean Perrin, professor at the Sorbonne. ("Les Atomes," 5th edit., 1914.)

If an aqueous suspension of **gamboge**, a gum-resin familiar to painters in water-colour, is examined under the microscope, the particles are seen to be in motion. Each particle performs little excursions in an apparently erratic manner, moving in a zigzag path. This motion was first observed with grains of pollen suspended in water by the botanist Robert Brown in 1827 ; it is shown by all suspensions, if the particles are sufficiently small, and is known as the **Brownian movement.**

The **cause of the Brownian movement** was ascribed to molecular bombardment of the suspended particles, by the molecules of the liquid, by C. Wiener in 1863. This was confirmed by Svedberg in 1906 ; he found that the length of the path described agrees with that calculated from the kinetic theory by Einstein (1905), and by Smoluchowski (1906).

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Perrin found that if the emulsion of gamboge was allowed to settle, the particles did not fall flat to the bottom of the vessel, but remained as a minute haze, extending only over a fraction of a millimetre, exhibiting the Brownian movement, and diminishing rapidly in density with the height. This was exactly analogous to the diminution in density of the atmosphere ; in the latter, on account of the small weight of the gaseous molecules, a height of some hundreds of miles is necessary to get the same gradation in density as is evident in less than a millimetre with the comparatively massive gamboge particles. The gamboge particles and the gaseous molecules are equally supported against the action of gravity by their kinetic energies. By counting the numbers of particles at different heights under the microscope (Fig. 173) it was possible to find the law of distribution at different heights.

If n and n' are the numbers of gamboge particles per c.c. at two heights h cm. apart, then, if the "solution" obeys the gas laws, the osmotic pressures, p and p', are in the ratio of n to n'. The ratio p/p', however, will be connected with the height h by the well-known logarithmic formula giving the diminution of barometric pressure with the height. The distance h required to produce a given fall of pressure is inversely proportional to the density, or molecular weight, of the gas. To halve the density (or pressure) in an oxygen atmosphere, a vertical ascent of 5 kilometres is required; in hydrogen, with lighter molecules, the ascent is $5 \times 16 = 80$ km., whilst with carbon dioxide, with heavier molecules, it is only $5 \times 16/22 = 3{\cdot}63$ km. The "molecular weight" of the gamboge particles could thus be calculated from the height in which the number per c.c. is halved. The weight of each particle of gamboge was found by counting the number per c.c., and finding the total weight per c.c. The number of particles required to make up the molecular weight could thus be calculated. This was found to be $\mathbf{N} = \mathbf{6 \times 10^{23}}$, which is the same as the value of **Avogadro's constant** for a gas.

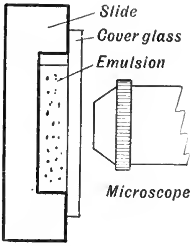

FIG. 173.—Perrin's Experiment with Gamboge Emulsion.

The suspended particles in the gamboge emulsion, therefore, obey the gas laws. It seems very probable that the particles in true solutions, which are much more closely similar to those of gases, should also obey the gas laws, and that osmotic pressure is caused by molecular bombardment. A partition allowing only water molecules to pass through, and arresting gamboge particles, would be subjected to a feeble bombardment by the latter, and experience a small osmotic pressure. In the case of true solutions, the number of molecules in a given space is much larger and the pressure is correspondingly greater.

By examining the Brownian movement of the suspended particles in tobacco-smoke, de Broglie found $\mathbf{N} = 6{\cdot}43 \times 10^{23}$.

Liquid diffusion.—Liquid diffusion, mentioned on p. 258 as evidence of molecular motion, was investigated by Graham (1850–62). He placed small bottles, containing solutions of various substances, in large jars of water (Fig. 174), and determined by analysis the amount of substance diffusing into the water in a given time.

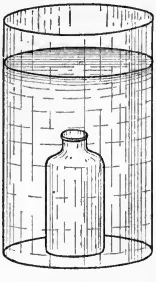
FIG. 174. Graham's Experiment on Liquid Diffusion.

By using apparatus of the same dimensions, he was able to obtain comparative results, and found that the rates of diffusion differed considerably. Acids and salts diffused fairly quickly, whereas glue, starch, and albumin diffused only very slowly. The rapidly diffusing substances were (except acids) all crystalline in the solid state, and were called **crystalloids** by Graham. Gum and albumin, however, form amorphous solid masses resembling glue, and were called **colloids** (Greek *kollos*, glue). The differences were so great that Graham considered himself justified in differentiating between "two worlds of matter, the crystalloid and the colloid," each with characteristic properties.

Substance.	**Times of equal diffusion.**	**Amounts diffusing in equal times.**
Sodium chloride	100	100
Ammonia	60	85
Alcohol	200	47
Glucose	300	36
Gum arabic	700	0·8
Albumin	2100	0·03

Dialysis.—In another set of experiments Graham placed the solution in a shallow bell-jar, the bottom of which was closed by a piece of parchment paper or bladder (*i.e.*, a solid colloid). This membrane separated the solution from pure water, in which the apparatus, called a **dialyser** (Fig. 175), was placed. Crystalloids passed readily through the colloidal septum, whereas colloids were either arrested or diffused exceedingly slowly.

By means of the dialyser a solution of a colloid may be freed from crystalloidal impurities (*e.g.*, salts). A convenient dialyser consists of a parchment paper tube (prepared by treating unglazed paper with concentrated sulphuric acid, and washing), bent into a U-shape, filled with the solution, and placed in a jar of distilled water, which is frequently

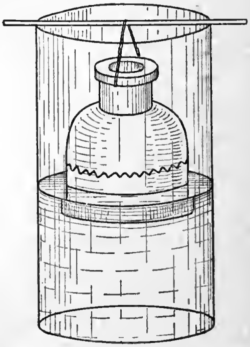
FIG. 175.—Graham's Dialyser.

renewed (Fig. 176). Small "thimbles" of parchment paper, slipped over the end of a glass tube, and fixed by a short length of rubber tubing, may also be used. Collodion films (p. 570) are still more efficient.

EXPT. 122.—Pour a solution of potassium iodide and starch into a dialyser, consisting of a piece of parchment paper tied tightly over the mouth of a bell-jar. Suspend the bell-jar with the parchment paper dipping into distilled water in a dish. After half an hour add chlorine water to the water in the dish. A yellow colour, due to liberated iodine, shows that the iodide has diffused through the parchment paper, but the starch is retained, since this would have given a blue colour with the iodine, as may be seen by adding chlorine water to the liquid in the bell-jar.

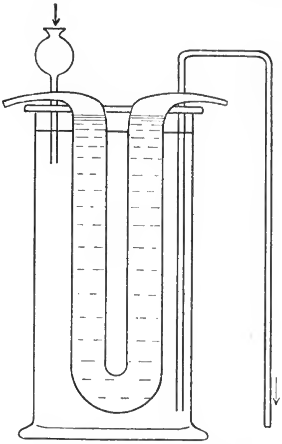

FIG. 176.—Tubular Dialyser.

All the experimental data show that **the transition from crystalloids to colloids is gradual,** depending on the size of the particles; suspensions of gold may be prepared which range from microscopically heterogeneous, through colloidal solutions (ultra-microscopically heterogeneous), to true solutions, with increasing fineness of the particles from 10^{-5} cm. to 10^{-8} cm.

The sharp differentiation between crystalloids and colloids made by Graham has thus not been confirmed. Albumin may be obtained in a crystalline form, and crystalline substances, such as common salt, may be prepared in the form of colloidal solutions by precipitation in liquids (*e.g.*, ether) in which they do not form true solutions. The real factor determining whether a substance forms a colloidal solution or a true solution is the size of the dispersed particles (p. 8); it is more correct to speak of the **colloidal state of matter** than of "colloidal substances." Even carefully filtered solutions of cane-sugar show a slight Tyndall effect with a beam of light (p. 7), although this is very much less than that obtained with colloidal solutions, which contain larger particles. Lord Rayleigh showed that the blue colour of the sky, which was formerly attributed to the scattering of light by suspended dust, could be accounted for by the scattering effect of the gaseous molecules of the atmosphere.

Molecular weights of colloids.—Organic colloids must have **high molecular weights**; thus, gum arabic, although possessing the empirical formula $C_{12}H_{11}O_{11}$, is acidic, and the very small amount of base required for its neutralisation shows that its molecule is much more complex . $(C_{12}H_{11}O_{11})_7$. By the method of **depression of freezing point** applied to other colloidal solutions, high molecular weights have also been found : starch, 25,000 ; tannin, 1100 ; silicic acid (p. 745), 49,000 ; rubber (in benzene), 6500. The slowness of diffusion and dialysis is readily understood when one considers that with such enormous molecules (often ultra-microscopically visible) the molecular movement must be very slow, since the square of the velocity is inversely proportional to the molecular weight. The **osmotic pressures** of colloidal solutions are, as would be expected from the large molecular weights, very small, but they appear to be definite. Pfeffer obtained the following values with 1 per cent. aqueous solutions :

	Pressure cm. Hg.	Molecular weight.	
Potassium nitrate	178	—	
Cane-sugar ...	47	342	
Dextrin	16·5	975	
Gum arabic ...	7·2	2230	$[(C_{12}H_{11}O_{11})_7 = 2317]$

Since the molecular weights are inversely proportional to the osmotic pressures (except in the case of potassium nitrate, which is an electrolyte and is abnormal, as will be shown later), the figures in the third column may be calculated from the osmotic pressures and the molecular weight of cane-sugar = 342.

Linebarger (1892), using a parchment-paper membrane, found the molecular weight of colloidal tungstic acid, by the osmotic method, to be 1720, which corresponds with $(H_2WO_4)_7 = 1750$.

Graham's suggestion that colloids as a class have **high molecular weights,** and **complex molecules,** possibly formed by the association of a number of crystalloid molecules (*e.g.*, in the case of tungstic acid), has therefore been confirmed.

The molecular weights of colloids have also been determined from the **rate of diffusion ;** the latter is inversely proportional to the square-root of the molecular weight. In this way Herzog (1908) found the molecular weight of albumin to be 17,000 ; Sabanejeff and Alexandroff found 13,000—14,000 by the freezing - point method. The satisfactory agreement in this and other cases, between results obtained by different methods, seems to indicate that colloids possess definite molecular weights, which may, of course, vary with the method of preparation.

Electrolytes.—In a large number of cases, the molecular weights of dissolved substances are found to be the same as those deduced from the vapour densities. When the substance is not volatile, it often corresponds with the simplest molecular formula—*e.g.*, cane-sugar, $C_{12}H_{22}O_{11}$. Solutions of organic substances in water, alcohol, and ether usually show **normal** molecular weights. Raoult, however, observed that many substances dissolved in benzene, nitrobenzene, and ethylene dibromide gave depressions of freezing point, or lowerings of vapour pressure, only half the normal, and he explained this by the **association** of the solute to form double molecules. Many such substances in fact (*e.g.*, acetic acid) gave abnormally high vapour densities. An abnormally small depression is also produced when the dissolved substance crystallises out with the solvent to form a *homogeneous* solid solution (p. 94); the freezing point may thus even be *elevated.*

But when aqueous solutions of acids, bases, and salts, (*i.e.*, **electrolytes**) were found to give molecular depressions considerably in excess of the normal, which increased with dilution until they approached double the normal depression in most cases, or an even higher multiple in others, the interpretation was by no means clear. It might indeed be supposed that all the so-called normal depressions produced by organic solutes were really due to double molecules, and that acids, bases, and salts are normal, but the identity of the values of the gas constant R from measurements of gaseous density and osmotic pressure, together with the whole body of experimental evidence, tells unmistakably against this hypothesis. The only other explanation possible, if we regard the laws of solution as valid in all cases, is to suppose that the **salts are dissociated in solution.** The molecules must then break up into sub-molecules, and at high dilution the dissociation must be practically complete. This, however, is exactly the state of affairs postulated by Arrhenius in 1887 in his theory of **electrolytic dissociation** (p. 283). The sub-molecules are the electrically charged **ions**: $KCl \rightleftharpoons K^{\cdot} + Cl'$, and the increase in the number of molecules of solute so produced accounts for the abnormally large depression of freezing point. The ions, in fact, behave in respect to depression of freezing point exactly like neutral molecules. The electrolytic dissociation theory, therefore, not only gave a clear explanation of the facts of electrolysis, as discovered by Faraday, but cleared away in one stroke the perplexing difficulties which had surrounded the properties of solutions of electrolytes as investigated by Raoult.

Relations between different methods for the determination of molecular weights of dissolved substances.—At first sight it would seem that no two sets of phenomena could be less related than the osmotic pressure and the freezing point, or vapour pressure, of solutions. It has been well said, however, that the business of science is to bring out unsuspected relations between phenomena, and Newton's demonstration that the tides, and the fall of an apple from a tree, are two expressions of an identical force operating in Nature is only one of the many cases which could be cited in this connection. In 1886 Van't Hoff was able to show that the osmotic pressure, vapour pressure, and freezing point of a solution are closely connected, so that if one is given the others may be calculated without knowing anything beyond the properties of the *pure solvent.* Thus, the depression of freezing point and the lowering of vapour pressure may be calculated from the latent heat of fusion, or of evaporation, and the freezing, or boiling, point of the pure solvent, respectively, quite independently of the nature of the dissolved substance. The three methods are interconnected, and *necessarily* give the same results. It follows that the values of the degree of ionisation of an electrolyte determined by all three methods must be identical, and their agreement is, in itself, no proof of the validity of the theory of electrolytic dissociation. On the other hand, the **conductivity** (p. 291) is an entirely independent method of finding the ionisation, and the agreement between the value so found and that found by any or all of the other three methods, affords a very valuable confirmation of the ionisation hypothesis.

Substance.	Concentration gm. mol./litre.	Ionisation from conductivity.	Ionisation from freezing point.
NaCl ...	0·001	98·0	98·4
	0·01	93·5	90·5
	0·1	84·1	84·1
K_2SO_4 ...	0·001	92·3	94·2
	0·005	85·8	88·7
	0·05	70·1	72·6
HCl ...	0·002	100·0	98·4
	0·01	98·9	95·8
	0·1	93·9	88·6

SUMMARY OF CHAPTER XVII

The **freezing point** of a solvent is lowered by a dissolved substance, and the depression, D, is proportional to the amount of substance, m, in 1 kgm. of solvent. The **molecular lowering,** Δ, for the molecular weight, M, in 1 kgm. of solvent, is constant for all substances (except electrolytes, and associated substances) in a given solvent, when the solution is dilute. Thus, it follows that $m : M :: D : \Delta$, or $M = m\,\Delta/D$.

The **boiling point** of a solvent is raised by a dissolved substance, and the same laws hold as for the freezing point: $M = mE/D$, where E is the **molecular elevation** of boiling point.

The **vapour pressure** of a liquid is lowered by a dissolved substance. If n gm. mol. of the substance are dissolved in N gm. mol. of solvent, and if f_0, f are the vapour pressures of the pure solvent and solution, respectively, then $(f_0 - f)/f_0 = n/(N+n)$.

The above relations enable one to determine the **molecular weight** of a substance in solution.

The **osmotic pressure** of a dissolved substance is related to the concentration and temperature of the solution in the same way as the pressure of a gas.

Colloidal solutions show only small differences from the freezing- and boiling-points of the solvent, and small osmotic pressures. The colloidal substance has, therefore, a high molecular weight.

EXERCISES ON CHAPTER XVII

1. What methods may be used to determine the molecular weight of a substance in solution ? Describe carefully how you would find the molecular weight of dissolved cane-sugar by any one of these methods.

2. Describe the cases of abnormal depression of freezing point which are met with. What explanations have been given of these results ?

3. What is meant by osmotic pressure ? How have osmotic pressures been measured, and of what theoretical value are the results ?

4. Van't Hoff (1886) stated that "dissolved substances obey the gas laws." On what experimental evidence is this statement based ? Show, from the results for the osmotic pressures of dilute solutions of cane-sugar (p. 310), that these may be summarised in the formula $PV = RT$, where P = osmotic pressure, V = volume containing 1 gm. mol., and that R has the same value as for a gas (p. 149).

5. A solution of 9·21 gm. of mercuric cyanide, $Hg(CN)_2$, dissolved in 100 gm. of water has a vapour pressure at 100° of 755·2 mm. Find the molecular weight of the dissolved salt. What inference may be drawn as to the electrolytic dissociation of mercuric cyanide in water ?

6. A solution of 9·472 gm. of cadmium iodide, CdI_2, in 44·69 gm. of water boils at 100·303°. What is the molecular weight of dissolved cadmium iodide ?

7. A solution of lithium chloride containing 4·13 gm. per litre of water freezes at $-0·343°$. What is the degree of ionisation ? The limiting equivalent conductivity of lithium chloride (p. 291) is 98·9: what is the conductivity of the above solution ?

8. What is the Brownian movement ? Give a short account of Perrin's researches on the phenomenon, and point out the importance of the results to the theory of solutions.

9. In what respects do crystalloids differ from colloids ? To what extent do you consider that Graham's sharp differentiation of the two as "separate worlds of matter" is justified ?

10. A solution of 24·67 gm. of colloidal tungstic acid per litre gave an osmotic pressure of 25·2 cm. of mercury at 17°. Find the molecular weight. What formula does this indicate (tungstic acid is H_2WO_4) ?

11. Explain what is meant by dialysis: how would you separate a mixture of common salt and albumin ?

CHAPTER XVIII

OZONE

The formation of ozone.—Van Marum in 1785 noticed that the air in the vicinity of an electrical machine in active operation acquired a peculiar smell, and tarnished mercury. Cruickshank in 1801 observed the same smell in electrolytic oxygen, but the fact that the odour was due to a peculiar gas was only recognised in 1840 by Schönbein, who gave the substance the name **ozone** (Greek *ozo*, I smell). He found that it is also produced by the slow oxidation of phosphorus in moist air, and is capable of liberating iodine from potassium iodide.

Expt. 123.—Place a few sticks of freshly scraped phosphorus in a stoppered bottle with a little water. When the fumes have subsided, introduce a piece of paper dipped into a solution of potassium iodide and starch (" starch-iodide paper "). This is at once turned blue. The peculiar smell of the gas is also noticeable. The ozonisation is most pronounced at 24° ; below 6° no action occurs, except under reduced pressure. A greenish, phosphorescent light, which can be seen in the dark, accompanies the formation of ozone.

Ozone is said to occur in traces in country, especially sea, air, but many of the effects attributed to ozone are doubtless caused by hydrogen peroxide, or oxides of nitrogen. There is some spectroscopic evidence for the existence of ozone in the upper atmosphere, where it may be formed by the action of ultra-violet light on oxygen. It has been stated that the maximum amount of ozone in the air never exceeds 1 in 450,000. The evaporation of salt-water in the form of spray is said to produce the ozone of sea air. If present in larger amounts than 1 in 20,000, ozone in air has an irritant action on the mucous membrane, and is poisonous.

Ozone is produced, apart from the action of the electrical discharge, and the slow oxidation (autoxidation) of phosphorus in air, in many other reactions, in most cases in small amounts.

It is contained in electrolytic oxygen, and in the oxygen evolved by the action of fluorine on water, by the action of concentrated sulphuric acid on barium peroxide, potassium permanganate, and potassium dichromate. It is produced by passing oxygen over heated manganese dioxide, by the action of radium salts on oxygen, and by heating ammonium persulphate with nitric acid.

EXPT. 124.—Warm a little potassium dichromate with concentrated sulphuric acid, and test the gas with KI-starch paper.

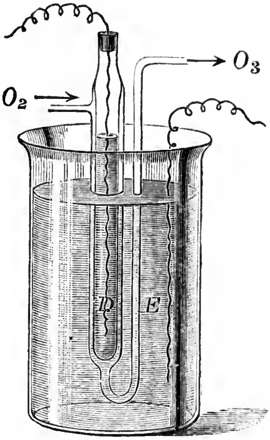

FIG. 177.—Brodie's Ozoniser.

Ozone is formed in traces in flames of burning hydrogen, or coal-gas, but not by the combustion of carbon or carbon monoxide. It was previously supposed to be formed by the slow combustion of ether vapour, but the substance produced is probably hydrogen peroxide. Ozone is given off on heating crystalline periodic acid, and by exposing oxygen to ultraviolet light, or radium emanation.

In all cases, ozone is obtained mixed with oxygen in varying amounts: the product is **ozonised oxygen** (or ozonised air).

The preparation of ozone.—The most convenient method of preparing ozonised oxygen is by the action of an **electric brush-discharge** on oxygen, preferably dry. Many types of apparatus are used for this purpose, but they are all very similar in principle. One of the most useful is probably that of Brodie (1872) (Fig. 177).

EXPT. 125—The oxygen is passed slowly through the annular space between two glass tubes, the inner tube, *D*, being filled with concentrated sulphuric acid or copper sulphate solution, and the whole apparatus placed in a jar, *E*, of the same liquid. The two wires from a good Ruhmkorff coil dip into the two liquids, which form electrodes, and at the same time serve to cool the apparatus. A bluish-violet glow is seen in the glass surfaces, accompanied by a hissing noise; there should be very few sparks, as these destroy ozone. The gas is conducted away through glass tubes with ground-glass joints, or joints made with paraffin wax or ordinary corks (Fig. 178). Rubber is very quickly destroyed by ozone, dry cork is more resistant. Air may be used instead of oxygen,

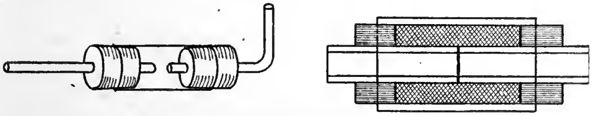
FIG. 178.—Joints for Ozone Apparatus.

but less ozone is obtained, and nitrogen pentoxide may then be present in the gas. (The original ozoniser of Siemens [1858] (Fig. 179) consists of two concentric glass tubes, the outer covered, and the inner lined, with tinfoil, but the type just described is superior in many ways.)

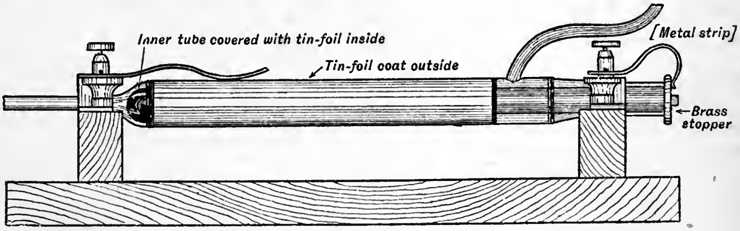

FIG. 179.—Siemens' Ozoniser.

By cooling the oxygen to 0°, using a powerful coil, and avoiding sparks, as much as 25 per cent. of the oxygen may be converted into ozone; usually the yield is much less.

EXPT. 126.—Ozonised oxygen is formed by the electrolysis of sulphuric acid (sp. gr. 1·1). The apparatus is shown in Fig. 180. A very good yield is obtained with a heavy current and an anode (positive electrode) composed of a narrow platinum tube coated with glass, having a narrow line of metal exposed, and cooled by a stream of calcium chloride solution at − 14° passing through.

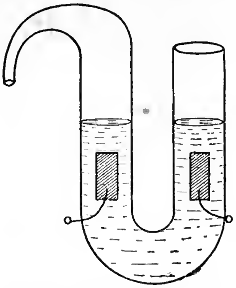

FIG. 180.—Ozone from Sulphuric Acid by Electrolysis.

Ozone is formed in fairly large quantities when oxygen (or air) is exposed to ultra-violet light. If a quartz mercury lamp is operated under a glass bell-jar for a few minutes, the air in the jar smells strongly of ozone. Liquid oxygen exposed to ultra-violet light becomes dark blue in colour, owing to the production of liquid ozone (p. 328).

The composition of ozone.—Schönbein found that if ozonised oxygen is passed through a glass tube heated to 400°, it loses its smell and action on KI-starch paper, and the gas then appears to be ordinary oxygen.

EXPT. 127.—Attach a piece of hard glass tube by a cork joint to the ozoniser, and heat the tube with a Bunsen flame. The issuing gas no longer acts on KI-starch paper.

Marignac and de la Rive (1848), and Shenstone and Baker (1908), found that pure dry oxygen can be ozonised by an electric discharge. Briner and Durand (1908) converted a confined volume of oxygen *completely* into liquid ozone by the silent discharge in a tube of dry oxygen, cooled in liquid air. Thus, **ozone is merely a modification of oxygen.**

This conclusion was also reached by Andrews (1856), who dried electrolytic oxygen by means of sulphuric acid, and then passed it through two bulb-tubes (Fig. 181) containing potassium iodide solution, and concentrated sulphuric acid, respectively. The increase in weight of the two bulbs was exactly equal to the oxygen equivalent ($O = I_2$) of the iodine liberated. The iodide bulb was then replaced by a glass tube heated to 400°. The weight of the sulphuric acid bulb remained constant, showing that the gas contained no hydrogen. Andrews also found that ozone prepared in different ways (electric discharge, electrolysis, autoxidation of phosphorus) has the same properties.

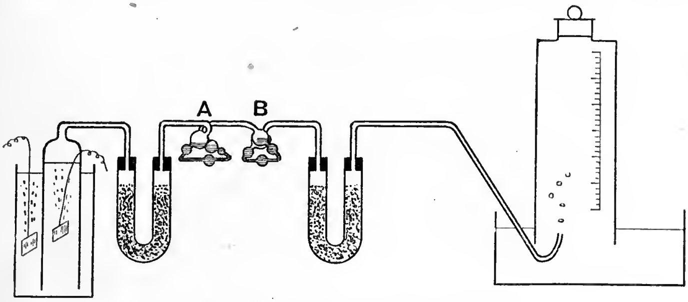

FIG. 181.—Andrews' Experiments on Ozone.

The formula of ozone.—If ozone is a modification of oxygen, it must have the formula O_n. Andrews and Tait (1860) first attempted to find the formula of ozone. They filled a tube, *A* (Fig. 182), with dry oxygen, which communicated with a sulphuric acid manometer, *B*. Sulphuric acid is without action on ozone. On sparking the oxygen, a maximum contraction of one-twelfth was observed. When the tube was heated to 300°, the original volume was restored. A glass bulb of mercury broken inside the tube by means of a short length of glass rod which could be shaken on it, was converted into a black powder, and the original volume of gas was again recovered. A bulb of potassium iodide solution broken in the

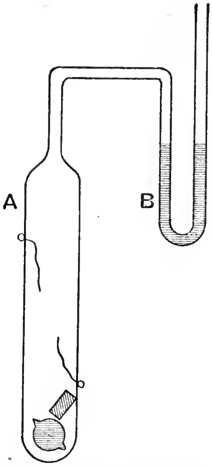

FIG. 182.—Andrews and Tait's Experiments on Ozone.

gas produced iodine, but in this case the volume of the gas remained unchanged, although it no longer expanded after heating to 300°, and was therefore completely converted into oxygen.

One possible explanation of the constancy of volume of the gas when the ozone is destroyed by potassium iodide, is that the ozone is distributed in the gas in the form of a finely-divided solid, occupying practically no volume. A more rational explanation is that at the same moment as one portion of ozone reacts with the iodide another portion changes into ordinary oxygen, the expansion due to the second change being exactly equal to the contraction due to the first. In any case, ozone is apparently denser than oxygen.

Odling, in 1861, pointed out that the reactions could be explained on the assumption that the formula of ozone is O_3:

$$2KI + O_3 \text{ (1 vol.)} + H_2O = 2KOH + O_2 \text{ (1 vol.)} + I_2.$$

The formula O_{2+n} will obviously give the same result, but O_3 is the simplest, and there were no experiments pointing to a more complicated formula.

Odling's formula was confirmed by Soret in 1866–8 by two sets of experiments.* Soret pointed out that oxidisable bodies which destroy ozone without change of volume, such as those used by Andrews and Tait, give no indication of the real density of ozone. Thus, suppose that 100 vols. of oxygen after electrisation contract to 90 vols. Assume that 100 vols. contain 100 O_2 molecules, then the contracted gas must contain 90 molecules of (O_2 + ozone).

This change of volume can be explained by numerous formulæ for ozone, since the only condition to be satisfied is that the 90 volumes, after heating, shall expand again to 100 volumes. This is the case, for example, with the following formulæ:

$$\overbrace{\begin{array}{cc} 70O_2 & 70O_2 \\ 20O_3 & 30O_2 \\ \hline 90 & 100 \end{array}}^{O_3} \qquad \overbrace{\begin{array}{cc} 80O_2 & 80O_2 \\ 10O_4 & 20O_2 \\ \hline 90 & 100 \end{array}}^{O_4} \qquad \overbrace{\begin{array}{cc} 89O_2 & 89O_2 \\ O_{22} & 11O_2 \\ \hline 90 & 100 \end{array}}^{O_{22}}$$

In order to find the relative volume of ozone in the mixture, some solvent or absorbent is evidently necessary which takes up the whole of the ozone without liberating oxygen (as is the case with potassium iodide). By comparing the **contraction on absorption** with the **expansion on heating** it would then be possible to distinguish between the above cases.

Thus, if the formula is O_3, the contraction on absorption is 20,

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* *Eau oxygénée et ozone,* in "Classiques de la Science" (III), pub. A. Colin, Paris, 1913.

whilst the expansion on heating is 100 -- 90 = 10. If the formula is O_4, the contraction is 10 and the expansion is 10 ; if the formula is O_{22}, the contraction is 1 and the expansion is 10. **The formula O_3 thus requires that the contraction on absorption shall be double the expansion on heating.**

Soret found that suitable absorbents for ozone were certain essential oils, such as oil of cinnamon and oil of turpentine. He took two flasks, of 250 c.c. capacity, with graduated necks, filled with ozonised oxygen and inverted over water (Fig. 183). In one flask the ozone was absorbed by turpentine, when dense white fumes were produced ; in the other it was decomposed by heating the flask by a flame. The contraction in the first flask was found to be almost exactly double the expansion (after the gas had cooled) in the second. Thus, Odling's formula, O_3, was confirmed.

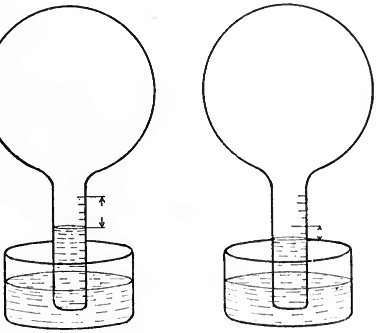


FIG. 183.—Soret's First Experiments on Ozone.

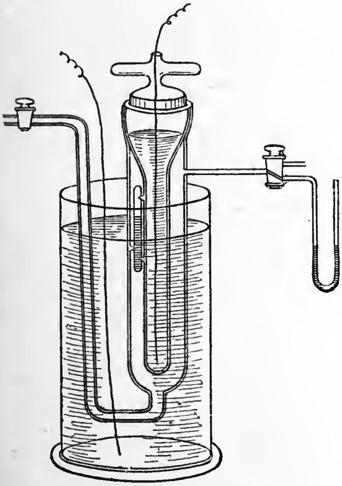


FIG. 184.—Absorption of Ozone by Turpentine.

EXPT. 128.—The apparatus shown in Fig. 184, devised by Newth (1896), may be used for this experiment. It consists of two concentric glass tubes, the inner tube fitted into the outer by a ground-glass stopper. The inner tube, and the glass jar in which the apparatus is placed, contain dilute sulphuric acid, and the two wires from the coil dip into the liquids as shown. By means of projections from the inner and outer tubes a thin glass tube containing oil of turpentine or oil of cinnamon is held in position in the annular space between them. A current of oxygen is passed through the apparatus, and the stopcocks are closed. The three-way stopcock is turned so as to put the manometer, containing concentrated sulphuric acid coloured with indigo, in communication with the apparatus, and the oxygen is ozonised. The contraction, after cooling, is read off on the gauge. The inner tube is then twisted, so as to break the tube of oil of cinnamon, and after absorption has occurred, the further contraction is read off. It will be found that the contraction on absorption is double the contraction on ozonisation, *i.e.*, double the expansion which would have occurred on decomposing the ozone by heat.

The density of ozone.—If pure ozone could be obtained, a determination of its **relative density** would allow us to confirm the formula O_3. But pure gaseous ozone has never been prepared, so that a different method has to be used. Soret, in a second research (1868), made use of **Graham's law of diffusion** (p. 191). If we compare the relative rates of diffusion of carbon dioxide (CO_2, density 22), ozone, and chlorine (Cl_2, density 35·2) into another gas, say oxygen, then if ozone has the formula O_3 (density 24) it should diffuse rather more slowly than carbon dioxide, but more rapidly than chlorine. The relative rates of diffusion are inversely proportional to the square roots of the densities :

$$\frac{\text{Rate of diffusion of } CO_2}{\text{Rate of diffusion of } O_3} = \frac{\sqrt{24}}{\sqrt{22}}; \quad \frac{\text{Rate of diffusion of } Cl_2}{\text{Rate of diffusion of } O_3} = \frac{\sqrt{24}}{\sqrt{35 \cdot 2}}.$$

In order to get over the difficulty of the dilution of ozone with oxygen, Soret measured the **relative diffusion,** v/V, of each gas mixed with oxygen, where v is the volume of gas diffusing and V the total volume present in the original mixture. The rate of diffusion of the oxygen in both directions was the same in all cases ; the rates of diffusion of the other gases were proportional to the numbers of molecules present in a given volume (measured by V), and inversely proportional to the square roots of the densities. The ratios v/V were therefore inversely proportional to the square roots of the densities of the diffusing gases.

The apparatus is shown in Fig. 185. It consisted of three glass tubes, *B*, *B′*, and *C*, placed over sulphuric acid in *E*, and separated by sliding glass plates with holes, as shown, so that the tubes could be put in communication or separated. *B′* was in every case filled with pure oxygen. *B* was first full of acid, and the mixture of one of the gases with oxygen, prepared in *C* in the proper proportions, was transferred to *B* by sliding the glass partition, *o*. The glass plates between *B* and *B′* had perforations, which could be brought between the two cylinders by sliding the plate *o′*. Diffusion from *B* to *B′* was allowed to go on for forty-five minutes, when the plate *o′* was slid back and the cylinders were again isolated. The gas in *B′* could then be driven out into a solution of baryta, when carbon dioxide was diffused, or potassium iodide, for chlorine or ozone. The ratio of the ozone in the original gas and in the gas in *B′* was determined from the ratio of the amounts of iodine liberated by equal volumes of the gases. If *u*, *u′* are the amounts of iodine liberated by the gas in B', and that remaining in B, respectively, then $v/V = u/(u + u')$. The relative rates of diffusion were thus found to be: chlorine, 0·227; ozone, 0·271; carbon dioxide, 0·290.

The ratio of these values for ozone and chlorine is 227/271 = 0·838. The inverse ratio of the square roots of the densities, assuming that ozone is O_3, is $\sqrt{24/35{\cdot}2} = 0{\cdot}824$. The diffusion ratio for carbon dioxide and ozone is 271/290 = 0·93, whilst the inverse ratio of the square roots of the densities, again assuming O_3 as the formula of ozone, is $\sqrt{22/24} = 0{\cdot}95$. The agreement is to 3 per cent., which is satisfactory when it is remembered that the ozonised oxygen contained only 5 per cent. of ozone by volume.

In 1898 Ladenburg repeated the experiments with nearly pure ozone, obtained by the fractionation of the liquid (p. 328). He compared the times of effusion of equal volumes of this gas and of oxygen in a Bunsen's effusion apparatus (p. 263), and found 430 secs. and 367·4 secs., respectively. The squares of the times of equal effusion are proportional to the densities (p. 191), hence $430^2 : 367{\cdot}4^2 :: x : 16$. Thus, $x = 22$. Since the gas contained a little oxygen, which would make the density lower, this result is sufficiently near the value 24, corresponding with O_3, to confirm the latter formula.

The formula O_3 for ozone was, however, completely established by a masterly research of Sir Benjamin Brodie in 1872. The description of this is too long to be given here, but the results confirmed Soret's less accurate values in every particular. All other formulæ were shown to be excluded.

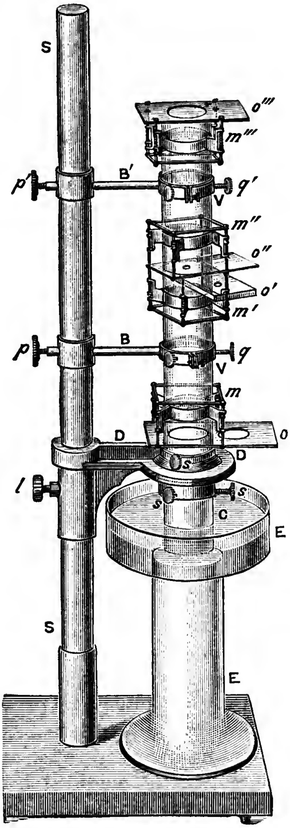


FIG. 185.—Density of Ozone by Diffusion (Soret).

The formula O_3 shows that ozone is an **allotropic modification** of oxygen (p. 114). The cause of allotropy in this case lies in the different molecular complexities. Ordinary oxygen has the formula O_2, whilst ozone contains three atoms of oxygen in the molecule, O_3. Both substances contain the same element, oxygen. Ozone is called a **polymer** of oxygen; the property of a substance existing in two or more forms of different molecular weights is called **polymerism.**

Stability of ozone.—Ozone contains considerably more **energy** (p. 387) than the oxygen gas from which it is produced: it is an **endothermic substance:** $3O_2 = 2O_3 - 2 \times 34$ kgm. cal. Like other endothermic substances (p. 390), it is **stable at high temperatures.** If oxygen is strongly heated, some ozone is produced: $3O_2 \rightleftarrows 2O_3$. Thus, at 6640°, there would, according to Nernst's calculations, be 10 per cent. of ozone in the equilibrium mixture. As the temperature falls the ozone rapidly decomposes, but if the hot gas is suddenly chilled, the rate of decomposition becomes so slow that the decomposition of the ozone, which is then really less stable than at higher temperatures, is arrested. Ozone is therefore produced in hydrogen or acetylene flames, or when a platinum wire or Nernst filament is strongly heated by an electric current, under liquid oxygen. This indicates a possible method for the manufacture of ozone.

The properties of ozone.—Ozonised oxygen, as usually prepared, does not contain more than 15 per cent. by volume of ozone. If the gas is cooled by passing it through a tube immersed in liquid oxygen, deep-blue **liquid ozone**, b. pt. −119°, condenses. On careful evaporation this gives a deep-blue gas, containing about 84 per cent. of ozone. The liquid is fairly stable below its boiling point, and may be distilled in the entire absence of dust or organic matter, the least trace of which, however, brings about its explosive decomposition. The gas is very unstable, exploding if warmed, or brought in contact with organic matter.

The decomposition of ozone in admixture with oxygen is slow at low temperatures: it is almost instantaneous at 300°, and takes place according to the equation $2O_3 = 3O_2$. It is accompanied by phosphorescence. Moisture slowly accelerates the decomposition: reduced pressure, chlorine, oxides of nitrogen, and phosphorus pentoxide, rapidly accelerate it.

Ozone is more soluble than oxygen in water. It is more soluble in glacial acetic acid, or carbon tetrachloride, than in water, forming blue solutions. It produces a remarkable effect on mercury: the meniscus of the latter is destroyed, and the metal adheres to glass in the form of a mirror. On shaking with water, the mercury recovers its original form. This reaction, which may be due to superficial oxidation, is very sensitive.

Expt. 129.—Pass ozonised oxygen into a clean flask containing a little mercury, and shake the flask. The mercury adheres to the sides of the flask in the form of a mirror.

Ozone is decomposed catalytically in contact with metallic silver, platinum, and palladium, and with oxides of manganese, cobalt, iron, lead, and silver. In the case of silver, the metal, if warm, is blackened, and an oxide is probably alternately formed and reduced : $2Ag + O_3 = Ag_2O + O_2$; $Ag_2O + O_3 = 2Ag + 2O_2$. The gas is decomposed by shaking it with powdered glass.

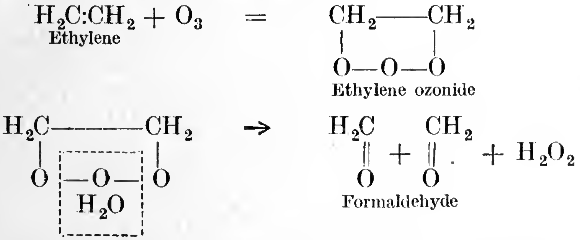
Barium peroxide, and hydrogen peroxide, react with ozone : $BaO \cdot \boxed{O + O} \cdot O_2 = BaO + 2O_2$, but the gas has no action on chromic acid or potassium permanganate (*cf.* H_2O_2). Sulphur dioxide is oxidised to the trioxide, the ozone being completely absorbed (Brodie) : $3SO_2 + O_3 = 3SO_3$. This is one of the few reactions in which the ozone molecule oxidises as a whole.

Ozone is a **powerful oxidising agent :** it bleaches indigo solution, and vegetable colours, and converts moist sulphur, phosphorus, and arsenic into their highest oxy-acids. It liberates halogens from their hydracids : $8HI + 2O_3 = 4H_2O + O_2 + 4I_2$. Ammonia is oxidised to white fumes of ammonium nitrite and nitrate ; a solution of potassium ferrocyanide is oxidised to ferricyanide :

$$2K_4FeC_6N_6 + H_2O + O_3 = 2K_3FeC_6N_6 + 2KOH + O_2.$$

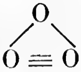
The liberation of iodine from potassium iodide constitutes a very delicate test for ozone, although iodine is liberated by other oxidising agents (*e.g.*, H_2O_2), by chlorine and bromine, and by higher oxides of nitrogen. The reaction with ozone is : $O_3 + 2KI + H_2O = O_2 + I_2 + 2KOH$; it occurs in a neutral solution, which then becomes alkaline. Moist iodine is oxidised to iodic acid, HIO_3 : $I_2 + 5O_3 + H_2O = 2HIO_3 + 5O_2$. Dry iodine is converted into a greenish powder, supposed to be I_4O_9, without change of volume of the gas : $2I_2 + 9O_3 = I_4O_9 + 9O_2$. An alkaline solution of potassium iodide is oxidised to iodate (KIO_3), and periodate (KIO_4).

Carbon compounds containing double linkages (p. 250) add on ozone to form unstable **ozonides,** which are decomposed by water with the formation of hydrogen peroxide :

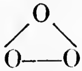


This reaction, in which compounds probably containing a chain of three oxygen atoms, —O—O—O—, are produced, points to the **structural formula**

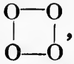
for ozone. The readiness with which the additional atom of oxygen is split off, leaving a residue of oxygen gas, O_2, led to the assumption that one atom in the ozone molecule was quadrivalent: $O{=}\overset{IV}{O}{=}O$. The formula

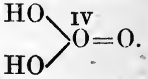


has also been proposed, but the simpler formula



is now regarded as the most probable (*cf.* the formula of hydrogen peroxide, p. 341).

The existence of closed rings of oxygen atoms containing four or more atoms: , is not impossible, and Harries (1911) thought that **oxozone,** O_4, was contained in ozonised oxygen, and that the later fractions of the gas obtained by the fractionation of liquid ozonised oxygen liberated more iodine from potassium iodide than corresponded with the density, and probably contained O_4. This has not been confirmed.

An aqueous solution of ozone reddens litmus paper before bleaching it, and has been supposed to contain **ozonic acid,** . By the action of ozone on solid caustic potash a yellow peroxide, K_2O_4, is obtained. This is regarded by Baeyer and Villiger as **potassium ozonate,** but on acidification it does not give ozone, but only oxygen and traces of hydrogen peroxide, H_2O_2.

Tests for ozone.—The difficulty of detecting ozone, when it is not present in sufficient concentration to exhibit its characteristic smell (1 volume in 500,000), is that hydrogen peroxide vapour (H_2O_2), and some oxides of nitrogen (N_2O_3,NO_2,N_2O_4), also liberate iodine from potassium iodide. Papers soaked in a solution of potassium iodide and starch are therefore of little value in the detection of ozone in the air, since the preceding compounds, and also chlorine (which liberates iodine from an iodide: $2KI + Cl_2 = 2KCl + I_2$), may be present. The lower oxides of nitrogen cannot exist in a gas simultaneously with excess of ozone, as they are at once oxidised to the pentoxide, N_2O_5, which forms nitric acid with moisture.

Test papers soaked in an alcoholic solution of **tetramethyl base** (tetramethyldiaminodiphenylmethane) are turned violet by ozone, straw-yellow by oxides of nitrogen, and deep blue by chlorine or bromine, but are unaffected by hydrogen peroxide. Paper impregnated with **benzidine** is coloured brown by ozone, blue by oxides of nitrogen, blue and then red by chlorine, but is not changed by hydrogen peroxide.

If one half of a piece of neutral litmus paper is moistened with potassium iodide solution, and exposed to a gas containing ozone, the wetted portion is turned blue, owing to liberation of alkali: $O_3 + 2KI + H_2O = O_2 + I_2 + 2KOH$. Oxides of nitrogen would not affect the wetted portion, but would turn the other half red, owing to the formation of nitrous and nitric acids with moisture. The iodine liberated by passing ozone through a *neutral* solution of potassium iodide may be titrated, after slight acidification, with sodium thiosulphate (p. 522), and the equivalent amount of ozone ($O_3 = I_2$) calculated. Another method of estimation depends on the oxidation of sodium nitrite solution by ozone: $NaNO_2 + O_3 = NaNO_3 + O_2$. Hydrogen peroxide and oxides of nitrogen are first removed from the gas by passing it through a solution of chromic acid. Hydrogen peroxide and ozone are destroyed by passing the gas through manganese dioxide, whilst oxides of nitrogen pass on, and will decolorise dilute permanganate solution. The latter solution, in turn, will absorb oxides of nitrogen, but allows ozone to pass through. Hydrogen peroxide is detected by bubbling the gas through a mixture of potassium ferricyanide and ferric chloride, which is turned blue (p. 340).

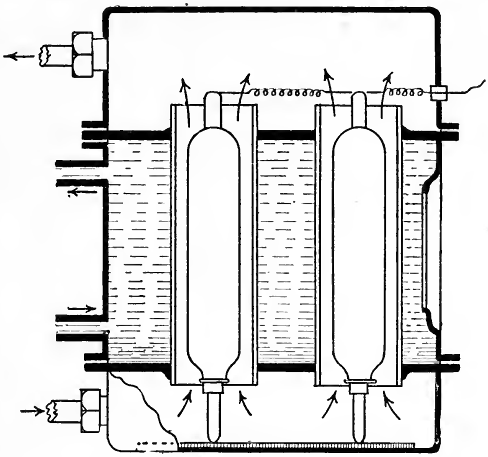


FIG. 186.—Siemens and Halske Ozoniser.

Manufacture and utilisation of ozone.—Air or oxygen is **ozonised** on the technical scale by exposure to brush discharges. The **Siemens and Halske ozoniser** (Fig. 186) consists of a battery of glass or porcelain tubes with internal tubes of aluminium, enclosed in an iron tank of water. This is earthed, and serves to cool the apparatus. The aluminium tubes are charged to a potential of 8000–10,000 volts, each battery of 6–8 tubes requiring half a kilowatt of power. The **Ozonair apparatus** consists of two sheets of aluminium gauze separated by a plate of the insulator "micanite," several units being enclosed in a case, and alternate plates charged and earthed. The best production amounts to about 40–60 gm. of ozone per kilowatt-hour of energy, at a concentration of 2 gm. of O_3 per cu. metre of air. With pure oxygen, 120–180 gm. are obtained. The yields are only about 5 and 15 per cent. of the theoretical with air and oxygen, respectively.

Ozonised air is used in the sterilisation of water, when it is bubbled through the filtered water in a tall column (2 gm. of ozone per cu. m. of water); for purifying air (*e.g.*, in the Central London Tube Railway); for oxidation processes (*e.g.*, *iso*-eugenol to vanillin), and its use for other purposes is in an experimental stage. The purification of water is its most important use: the plant supplying Paris deals with 24,000,000 gallons daily. A small plant is in operation at Knutsford, in Cheshire.

EXERCISES ON CHAPTER XVIII

1. In what reactions is ozone produced? How is the substance prepared (*a*) in the laboratory, (*b*) on the large scale? For what purposes is it used?

2. What experiments would you carry out to prove the following assertions: (*a*) ozone contains no element but oxygen; (*b*) ozone is a powerful oxidising agent; (*c*) the formula of ozone is O_3?

3. What is an endothermic substance? What do you know of the stability of ozone at high temperatures?

4. Describe, with equations, the action of ozone on (*a*) silver, (*b*) manganese dioxide, (*c*) potassium iodide, (*d*) potassium ferrocyanide, (*e*) caustic potash.

5. Give a brief account of the experiments which led to the adoption of the formula O_3 for ozone. What structural formulæ for the substance have been suggested?

6. One hundred c.c. of ozonised oxygen, when shaken with turpentine, contract to 85 c.c. What expansion will occur when 100 c.c. of the original gas is heated to 300°?

7. What tests would you apply to detect ozone in a gas? Point out what other substances might give these reactions, and say how you would distinguish them from ozone.

CHAPTER XIX

HYDROGEN PEROXIDE

Hydrogen peroxide, H_2O_2.—Barium monoxide or baryta, BaO, can absorb oxygen, forming a higher oxide, BaO_2, called **barium peroxide**. This is produced: (*a*) by passing a stream of oxygen over baryta heated to dull redness: $2BaO + O_2 \rightleftarrows 2BaO_2$; (*b*) by adding baryta to fused potassium chlorate, and washing out the soluble potassium chloride from the residue with water: $3BaO + KClO_3 = 3BaO_2 + KCl$ (soluble). The first method is due to Gay-Lussac and Thenard, the second to Liebig and Wöhler.

If barium peroxide is added to cold dilute hydrochloric acid, no oxygen is evolved; the solution contains barium chloride, and a new substance, **hydrogen peroxide**: $BaO_2 + 2HCl = BaCl_2 + H_2O_2$. Thenard, its discoverer (1818), called the latter *oxygenated water.*

The liquid acts as an **oxidising agent,** liberating iodine from a neutral, or acid, solution of potassium iodide: $2KI + H_2O_2 = 2KOH + I_2$. From the amount of iodine liberated, the proportion of hydrogen peroxide may be calculated.

In order to obtain a solution of hydrogen peroxide free from the soluble barium salt, the barium peroxide must be treated with an acid such as sulphuric, carbonic, or hydrofluosilicic (H_2SiF_6), which forms an insoluble barium salt. The latter precipitates, leaving an aqueous solution of hydrogen peroxide.

Expt. 130.—Stir up finely powdered barium peroxide with distilled water in a beaker, and pass a rapid stream of carbon dioxide through the suspension. After a few minutes add a solution of potassium iodide and starch: a blue colour is produced.

According to Merck, the above reaction should be carried out as described, not by adding the barium peroxide in small quantities at a time, when the particles become coated with insoluble barium carbonate. If excess of barium peroxide is used at once, the liquid remains alkaline until the end of the process, and decomposition is complete. An unstable **barium percarbonate,** $BaCO_4$, is first produced, which is then decomposed by water, producing barium carbonate and hydrogen peroxide: $BaO_2 + CO_2 = BaCO_4$; $BaCO_4 + H_2O = BaCO_3 + H_2O_2$.

Anhydrous barium peroxide is not easily decomposed by dilute sulphuric, or hydrofluosilicic, acid, on account of the formation of a coating of insoluble compounds on the particles of peroxide. A **hydrated barium peroxide,** $BaO_2,8H_2O$, is however, readily decomposed by these acids. It is prepared as follows.

Commercial barium peroxide, containing oxides of iron and aluminium, and silica, is finely powdered, and added a little at a time to a cold mixture of equal volumes of water and concentrated hydrochloric acid until the latter is neutralised. A little baryta solution is then added, which precipitates the iron and aluminium as hydroxides. These, together with the silica originally contained in the barium peroxide, are filtered off, and to the filtrate is added a saturated solution of barium hydroxide. A white, crystalline precipitate of hydrated barium peroxide is formed, which is filtered off, washed with cold water free from carbon dioxide, and kept moist in a stoppered bottle: (1) $BaO_2 + 2HCl = BaCl_2 + H_2O_2$; (2) $H_2O_2 + Ba(OH)_2 + 6H_2O = BaO_2,8H_2O$.

If this hydrated peroxide is treated with cold dilute sulphuric acid (1 vol. of acid : 5 vols. of H_2O), or with hydrofluosilicic acid, insoluble barium salts and a solution of hydrogen peroxide are produced: $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$, or $BaO_2 + H_2SiF_6 = BaSiF_6 + H_2O_2$.

If metallic sodium contained in a nickel boat is heated in a hard glass tube in a current of oxygen, the metal burns with a yellow flame, and a yellow mass of **sodium peroxide**, Na_2O_2, is left.

EXPT. 131.—Burn a small piece of sodium in a deflagrating spoon in a jar of dry oxygen. When the spoon is cold, dissolve the sodium peroxide in it by placing the spoon in water. Add dilute HCl, and a solution of KI and starch. A blue colour is produced: $Na_2O_2 + 2HCl = 2NaCl + H_2O_2$.

Sodium peroxide is now manufactured by heating sodium in a current of dry air, purified from carbon dioxide, and is a convenient source of hydrogen peroxide. The calculated amount of sodium peroxide is added, in small quantities at a time, to 20 per cent. sulphuric acid cooled in ice: $Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$. Two-thirds of the sodium sulphate separates as crystals of Glauber's salt, $Na_2SO_4,10H_2O$ and the liquid is then decanted and distilled *in vacuo* (see p. 336). Hydrogen peroxide is less volatile than water, so that the later fractions are collected. In this way Merck prepares a 30 per cent. solution of H_2O_2, known as **perhydrol.** It is preserved in stoppered bottles covered inside with paraffin wax.

More dilute solutions of hydrogen peroxide are prepared (usually from barium peroxide) for use in pharmacy. The strength of these solutions is stated in terms of the volume of oxygen evolved on heating, when the peroxide decomposes: $2H_2O_2 = 2H_2O + O_2$.

Commercial peroxide is usually "10 volumes," or "20 volumes," according as it gives off 10, or 20, times its volume of oxygen. Merck's preparation evolves 100 times its volume of oxygen: it is therefore sometimes (very improperly) called "100 per cent. peroxide."

From the equation: $2H_2O_2 = 2H_2O + O_2$, it is seen that 2×34 gm. of hydrogen peroxide evolve 32 gm. of oxygen, occupying 22·4 litres at S.T.P. Thus each gram of peroxide evolves 353 c.c. of O_2. A 1 per cent. solution therefore evolves 3·53 times its volume of oxygen; "10 vol." peroxide is therefore not quite 3 per cent. strength.

Concentration of solutions of hydrogen peroxide.—A dilute solution of hydrogen peroxide may be **concentrated** in several ways. If it is **frozen**, ice separates, and the residual liquid is therefore enriched in peroxide. It may also be concentrated by **evaporation** in a dish on a water-bath: hydrogen peroxide is appreciably less volatile than water. At a certain point, however, decomposition begins. The solution may then be placed in a flat dish in an evacuated desiccator containing concentrated sulphuric acid. When the solution has reached a certain concentration of peroxide, the latter begins to volatilise, but by working at low temperatures Thenard was able in this way to obtain a liquid (sp. gr. 1·452) giving off 475 vols. of O_2, *i.e.*, containing 95 per cent. of H_2O_2.

Hydrogen peroxide is very soluble in ether, so that if an aqueous solution is **extracted with ether** in a separating funnel (p. 14), most of the peroxide passes into the ethereal layer. The latter may be separated, and evaporated on a water-bath, when a concentrated solution of hydrogen peroxide in water is left.

These concentrated solutions decompose very easily on heating, or even at the ordinary temperature. They are rendered more stable by a trace of acid. Dilute aqueous solutions are fairly stable, especially if acidified.

More concentrated hydrogen peroxide may be obtained by distillation under reduced pressure; this method was also used by Thenard.

Pure hydrogen peroxide.—Until 1894, hydrogen peroxide was known only in the form of a more or less concentrated aqueous solution. In that year Wolffenstein obtained practically **pure hydrogen peroxide** by the **fractional distillation** of a concentrated aqueous solution under reduced pressure. He found that, under special conditions, hydrogen peroxide is fairly stable towards heat, viz., when it is free from (*a*) all alkaline substances, (*b*) every trace of heavy metal compounds, (*c*) all kinds of solid bodies, even of otherwise indifferent chemical character, *e.g.*, silica, alumina, etc. (The sodium sulphate in Merck's method of preparation (p. 334) is quite indifferent towards hydrogen peroxide.) By evaporating a 4·5 per cent. solution of the peroxide in a porcelain dish on a water-bath at 75°, he concentrated it to 66·6 per cent. Some peroxide was lost, not by decomposition, but by evaporation in the escaping steam, since it is distinctly volatile. This solution was shaken with ether, to precipitate alumina, and the ether evaporated from the filtered liquid on a water-bath. The strong hydrogen peroxide remaining was then distilled under the reduced pressure of 65 mm., and the fraction coming over between 81° and 85° collected. It contained 90·5 per cent. of H_2O_2. This was again fractionated under reduced pressure, and the fraction between 84° and 85° collected. It contained 99·1 per cent. of H_2O_2, and was free from all impurities.

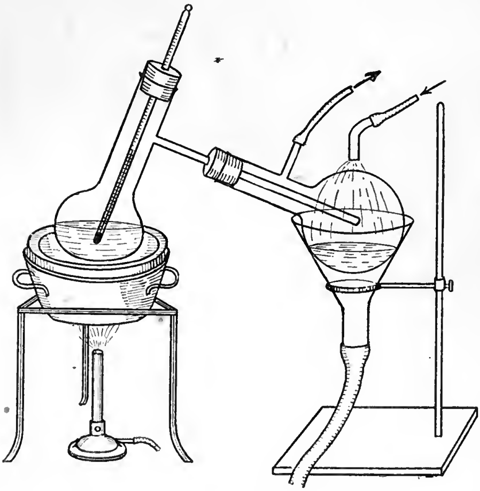


FIG. 187.—Distillation under Reduced Pressure.

The apparatus used for **distillation under reduced pressure** consists (Fig. 187) of a distilling flask, containing the solution of hydrogen peroxide, fitted with a thermometer, and placed on a water-bath. The side tube of this flask is fitted by a rubber stopper to the inside of a second distilling flask, which serves as a receiver, and is cooled by a stream of cold water. The side tube of this flask communicates by pressure tubing with a large empty bottle, which is connected with a good metal water pump, working on a high-pressure tap. A pressure gauge is connected with this bottle, and a three-way stopcock allows air to be admitted to the apparatus when the experiment is finished, so that the different parts may be disconnected, or when the receiver is changed during the operation. In the fractionation of hydrogen peroxide there is some danger of explosion, when the whole apparatus is shattered. This appears to be due to some extent to the formation of an unstable **ethyl peroxide,** $(C_2H_5)_2O_2$, discovered by Brodie, which is produced from the ether remaining in the peroxide after evaporation. It is safer to begin the experiment directly with Merck's 30 per cent. perhydrol, which has not been treated with ether.

Pure hydrogen peroxide is a clear, syrupy liquid, colourless in small amounts, but having a bluish colour like water when in bulk. It has an odour like that of nitric acid. It evaporates spontaneously in the air, boils at 84–85°/68 mm. or 69·2°/26 mm. Its specific gravity is 1·458 at 0°. The liquid has a strong **acid** reaction to litmus. In dilute solution (1·5 per cent.), however, hydrogen peroxide is completely neutral. By mixing the substance with water, and cooling in a mixture of solid carbon dioxide and ether, the crystalline **hydrates**: H_2O_2,H_2O, and $H_2O_2,2H_2O$, are obtained. The pure substance is fairly stable, and can be kept for several weeks in the absence of sunlight, provided the glass of the bottle is perfectly smooth. In contact with rough surfaces, or on shaking, decomposition occurs: $2H_2O_2 = 2H_2O + O_2$. Finely divided metals such as gold, silver, and platinum (but not iron) bring about explosive decomposition. Cotton-wool at once inflames. A mixture of magnesium, or carbon, powder with a trace of manganese dioxide at once inflames in contact with pure liquid H_2O_2.

On cooling 95–96 per cent. peroxide in solid carbon dioxide and ether, or in methyl chloride at − 23°, it solidifies to a hard crystalline mass. If a little of this solid is placed in the 95 per cent. solution cooled to − 10°, columnar prismatic crystals of pure **solid hydrogen peroxide**, melting at − 2°, are obtained. These crystals explode with a trace of platinum black; alone, they are fairly stable.

Solutions of hydrogen peroxide readily decompose spontaneously into water and oxygen in presence of traces of alkali. They become much more stable in presence of traces of sulphuric or phosphoric acids (hence the commercial peroxide is acid). The addition of alcohol, glycerin, or barbituric acid also renders the solutions stable. The vapour of hydrogen peroxide appears to be quite stable.

The chemical properties of hydrogen peroxide.—Hydrogen peroxide closely resembles ozone in many respects. It is an **endothermic compound**: $H_2 + O_2 = H_2O_2 - 45{\cdot}2$ kgm. cal. It is therefore **unstable** at the ordinary temperature, and, as in the case of ozone, one of the oxygen atoms tends to split off, with the formation of gaseous oxygen and water: $2H_2O_2 = 2H_2O + O_2 + 203{\cdot}2$ kgm. cal. This decomposition is seen to be attended with a very large evolution of heat, much greater than that which would be evolved in the decomposition into the elements: $2H_2O_2 = 2H_2 + 2O_2 + 90{\cdot}4$ kgm. cal. It is therefore the former reaction which actually occurs.

As in the case of ozone, the endothermic hydrogen peroxide is produced, and is stable, at high temperatures. If a hydrogen or carbon monoxide flame is allowed to impinge on the surface of cold water, ice, or solid carbon dioxide, hydrogen peroxide is found in the liquid. By rapid cooling, the hydrogen peroxide formed is chilled to a temperature at which its rate of decomposition is small before much decomposition at intermediate temperatures can occur.

Traces of hydrogen peroxide are formed by the direct union of hydrogen and oxygen when the mixed gases are passed over palladium-black: the water formed gives the reactions of the peroxide: $H_2 + O_2 = H_2O_2$. Small amounts are also formed by the action of bright sunlight, ultra-violet light, or radium emanation on water containing dissolved oxygen: or by the action of a brush discharge on a mixture of steam and oxygen, $2H_2O + O_2 = 2H_2O_2$. It is not produced by the spontaneous evaporation of water in air unless traces of zinc are present, although snow is said to contain it in traces. Minute quantities of hydrogen peroxide are formed in growing plants.

Expt. 132.—Allow a hydrogen flame to impinge on a piece of ice. Pour out the liquid produced, and add a little potassium iodide and starch solution: a blue colour indicates the presence of hydrogen peroxide.

Hydrogen peroxide is an **active oxidising agent**, the labile oxygen atom being easily split off, with formation of water. Arsenious and sulphurous acids are oxidised to arsenic and sulphuric acids: $H_3AsO_3 + H_2O_2 = H_3AsO_4 + H_2O$; $H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O$. Black lead sulphide is oxidised to white lead sulphate: $PbS + 4H_2O_2 = PbSO_4 + 4H_2O$, a reaction which is utilised in restoring discoloured oil-paintings, in which the white-lead pigment (basic lead carbonate) has become converted into black PbS by atmospheric sulphuretted hydrogen. Ferrous and manganous salts in neutral solution are converted into insoluble ferric oxide and manganese dioxide, respectively; from ferrous salts in acid solution ferric salts are formed: $2FeSO_4 + H_2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O$. This reaction may be used in the estimation of hydrogen peroxide. Benzene, in the presence of ferrous sulphate, is oxidised to phenol: $C_6H_6 + H_2O_2 = C_6H_5OH + H_2O$, and hydrogen peroxide is used as an oxidising agent in many organic oxidations when more energetic reagents would cause decomposition. Hydrogen peroxide also forms **molecular compounds** with many organic substances, and with some salts: $(NH_4)_2SO_4,H_2O_2$, $K_2CO_3,2H_2O_2$, Na_2HPO_4,H_2O_2. In these compounds it shows analogies with water of crystallisation.

Hydrogen peroxide is a feeble acid, much weaker than carbonic acid. With ammonia it forms directly the salt-like compounds, $NH_4 \cdot O_2H$ (ammonium hydrogen peroxide), and $(NH_4)_2O_2$ (ammonium peroxide). The compounds NaO_2H and Na_2O_2 are also known. The oxidising action of hydrogen peroxide is used in **bleaching** delicate materials (wool, silk, ivory, feathers) which would be injured by chlorine: the solution of the peroxide is made faintly alkaline with ammonia, or added to a 10 per cent. solution of sodium acetate. Hydrogen peroxide bleaches hair to a golden-yellow colour: it is called an *auricome* when used for this purpose. It is also a powerful antiseptic, and as it leaves no injurious products after its action, it is largely used as a gargle, etc. Hydrogen peroxide is used as an *antichlor* to remove excess of chlorine from bleached fabrics : $Cl_2 + H_2O_2 = 2HCl + O_2$.

Platinum black, and especially colloidal platinum (prepared by striking electric arcs between platinum wires under distilled water), bring about a rapid **catalytic decomposition** of hydrogen peroxide : $2H_2O_2 = 2H_2O + O_2$.

Expt. 133.—Add a little colloidal platinum to a solution of H_2O_2. There is a brisk evolution of oxygen. Stirring the liquid with a glass rod accelerates the reaction.

Liebermann (1904) considered that the platinum first absorbs atmospheric oxygen, rendering it "active," and the activated oxygen, probably in the atomic condition, then reacts with the labile oxygen atom of the peroxide : $H_2O \cdot \boxed{O + O} = H_2O + O_2$. Finely divided silver (see below), manganese dioxide, and other substances also cause the catalytic decomposition of H_2O_2.

In certain reactions hydrogen peroxide appears to function as a **reducing agent**. Thenard (1819) found that gold and silver oxides are reduced by it to the metals : $H_2O_2 + Ag_2O = H_2O + O_2 + 2Ag$.

Expt. 134.—Add caustic soda solution to a solution of silver nitrate : a *brown* precipitate of silver oxide is formed : $2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O$. Add H_2O_2 to this : it is at once converted into *black* metallic silver, with brisk evolution of oxygen. If a further quantity of H_2O_2 is added, it is *catalytically* decomposed by the finely divided silver.

Brodie (1850) showed that whenever hydrogen peroxide acts as a reducing agent, it is because the labile oxygen atom can withdraw another oxygen atom from the compound reduced, to produce a molecule of gaseous oxygen. Thus, it reacts (rather slowly) with ozone : $O_2 \cdot \boxed{O + O} \cdot H_2O = O_2 + O_2 + H_2O$.

Expt. 135.—Pour hydrogen peroxide (20 vols.) into a jar of ozonised air, replace the glass plate, and shake. After a time the odour of ozone disappears.

A solution of potassium permanganate acidified with sulphuric acid is readily reduced by hydrogen peroxide, with evolution of pure oxygen (p. 162) : $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$. This reaction may be used in the **estimation** of H_2O_2. Persulphates are also reduced : $K_2S_2O_8 + H_2O_2 = 2KHSO_4 + O_2$.

Manganese dioxide brings about an evolution of oxygen from a *neutral* solution of hydrogen peroxide, the action being apparently catalytic. In an *acid* solution the manganese dioxide is also reduced and a manganous salt is formed: $MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2$. Solutions of bleaching powder [calcium hypochlorite, $Ca(OCl)_2$], and sodium hypobromite also evolve oxygen: $NaOBr + H_2O_2 = NaBr + H_2O + O_2$. Iodine is liberated from acidified potassium iodide: $2KI + H_2O_2 + H_2SO_4 = K_2SO_4 + 2H_2O + I_2$. All these reactions are applied in the **estimation of hydrogen peroxide.**

Hydrogen peroxide acts powerfully on a photographic plate. The effects of traces of this substance have often been attributed to "rays."

An interesting case of the oxidising and reducing action of hydrogen peroxide was discovered by Brodie. An *acid* solution of potassium *ferro*cyanide is *oxidised* by hydrogen peroxide to potassium *ferri*cyanide: $2K_4FeC_6N_6 + H_2O_2 = 2K_3FeC_6N_6 + 2KOH$. An *alkaline* solution of potassium *ferri*cyanide, however, is *reduced* to potassium *ferro*cyanide by hydrogen peroxide: $2K_3FeC_6N_6 + 2KOH + H_2O_2 = 2K_4FeC_6N_6 + 2H_2O + O_2$. These changes may be followed by the reactions with iron salts described on p. 248.

Expt. 136.—Add some zinc to dilute sulphuric acid and ferrous sulphate solution in a flask through which a current of coal gas is passed. By means of a dropping funnel through the cork add a solution of $K_4FeC_6N_6$ in *boiled* water. A nearly white precipitate is formed. Now add ferrocyanide + H_2O_2: a deep blue precipitate is produced. H_2O_2 evolves oxygen from an alkaline solution of $K_3FeC_6N_6$.

Tests for hydrogen peroxide.—A very delicate **test** for hydrogen peroxide is the liberation of iodine from potassium iodide, giving a blue colour with starch. One part of peroxide in 25 million parts of water may be detected by this test. Other substances, such as ozone and nitrites, give this reaction, but hydrogen peroxide is the only substance which liberates iodine from potassium iodide in presence of ferrous sulphate. The reaction is: $2KI + H_2O_2 = 2KOH + I_2$.

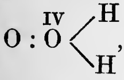
Another delicate reaction for hydrogen peroxide is the formation of a red coloration, due to titanium peroxide, TiO_3, with a solution of titanium dioxide in dilute sulphuric acid. This solution is prepared by heating TiO_2 with twice its volume of concentrated sulphuric acid, cooling, and diluting with ice-water.

Expt. 137.—If hydrogen peroxide is added to a solution of potassium dichromate acidified with dilute sulphuric acid, a brown colour is produced. If the solution is rapidly shaken with ether, the latter floats to the surface with a beautiful blue colour. An unstable **perchromic acid** is formed (p. 956), which dissolves in ether to form the blue liquid: this decomposes after a time, with evolution of oxygen, and a green, aqueous solution of chromic sulphate is formed in the lower layer.

Other tests are as follows: (1) guaiacol solution acidified with sulphuric acid gives a blue colour; (2) guaiacum tincture, with a little blood, gives a blue colour (this is also a delicate test for blood, and can be used in identifying blood-stains); (3) a mixture of aniline and potassium chlorate, dissolved in dilute sulphuric acid, gives a violet colour; (4) filter-paper soaked in a solution of cobalt naphthenate, and dried, changes from rose to olive-green with hydrogen peroxide.

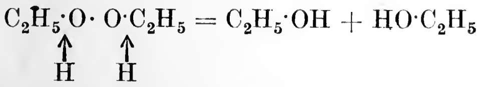
The formula of hydrogen peroxide.—The vapour-density of hydrogen peroxide has not yet been determined, but the molecular weight of the substance has been found from the freezing point of its aqueous solution (Carrara, 1893) to be 34, hence its formula is H_2O_2 (p. 302).

The **constitutional formula** may be written $H\cdot O\cdot O\cdot H$, *i.e.*, **dihydroxyl,** $HO\cdot OH$. This is in accordance with the **instability** of compounds which contain chains of directly linked oxygen atoms.

In order to account for the instability of one oxygen atom, which is readily split off, Kingzett (1884) assumed the formula to be , in which one atom of oxygen is quadrivalent. This is in agreement with the **acidic character** of the peroxide: it evolves carbon dioxide from a solution of sodium carbonate added to it drop by drop, forming sodium peroxide: $H_2O_2 + Na_2CO_3 = Na_2O_2 + H_2O + CO_2$. (If the peroxide is added to the carbonate, pure oxygen is evolved by catalytic decomposition.)

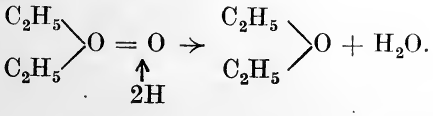
Brühl (1895), from the optical properties, suggested that both the oxygen atoms are quadrivalent: $HO\vdots OH$.

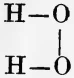
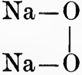
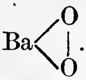
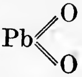
By the action of hydrogen peroxide on diethyl sulphate, $(C_2H_5)_2SO_4$, Baeyer and Villiger (1900) obtained **diethyl peroxide,** $(C_2H_5)_2O_2$, and **ethyl hydroperoxide,** $C_2H_5HO_2$. The former boils at 65° and is stable; the latter is violently explosive. By the action of zinc and acetic acid on diethyl peroxide it is reduced to ethyl alcohol, $C_2H_5\cdot OH$. This agrees with the formula $C_2H_5\cdot O\cdot O\cdot C_2H_5$:



$$C_2H_5\cdot \underset{\underset{H}{\uparrow}}{O}\cdot \ \underset{\underset{H}{\uparrow}}{O}\cdot C_2H_5 = C_2H_5\cdot OH + HO\cdot C_2H_5$$

Kingzett's formula, on the contrary, would require that ether, $(C_2H_5)_2O$, should be formed:



The formula of ethyl peroxide is therefore $C_2H_5{\cdot}O{\cdot}O{\cdot}C_2H_5$; that of ethyl hydrogen peroxide may be written $C_2H_5{\cdot}O{\cdot}OH$, and it is very probable that the formula of hydrogen peroxide is $H{\cdot}O{\cdot}O{\cdot}H$. It is therefore a **true peroxide,** containing two singly linked oxygen atoms :  $\begin{array}{r}H-O\\ |\\ H-O\end{array}$. Sodium peroxide is  $\begin{array}{r}Na-O\\ |\\ Na-O\end{array}$ and barium peroxide . True peroxides, which give hydrogen peroxide with acids, differ in constitution from the **dioxides** of lead, manganese, etc., which give only oxygen with concentrated acids, and chlorine with concentrated hydrochloric acid. Their formulæ are of the type : . This is confirmed by the formation of unstable higher chlorides on treatment with cold concentrated hydrochloric acid (p. 224); *e.g.*, $MnCl_4$ and $PbCl_4$. These form complex salts, *e.g.*, $(NH_4)_2PbCl_6$, ammonium chloroplumbate.

With hot concentrated hydrochloric acid, however, barium peroxide evolves chlorine : $BaO_2 + 4HCl = BaCl_2 + Cl_2 + 2H_2O$.

Autoxidation.—The formation of hydrogen peroxide during the slow oxidation of phosphorus, oil of turpentine, and metals, by gaseous oxygen in the presence of water, was studied by Schönbein in 1858. He found that the oxygen is equally divided in oxidising the substance (*e.g.*, lead) and in forming hydrogen peroxide : $Pb + O_2 + H_2O = PbO + H_2O_2$.

Schönbein considered that the oxygen molecule contained a positively and a negatively charged atom of oxygen, which he called *antozone* and *ozone*, respectively. The antozone formed hydrogen peroxide with water, or, if indigo solution or another oxidisable substance was present, it oxidised the latter.

It was found later that in many cases the first product is an unstable peroxide, which is decomposed by water with formation of a lower oxide, and hydrogen peroxide : $R + O_2 = RO_2$; $RO_2 + H_2O = RO + H_2O_2$. Turpentine, for example, forms a crystalline peroxide on standing in a loosely stoppered bottle.

According to Engler and Wild, the oxygen molecule is first opened up to form —O—O—, which combines with the **activator** (*e.g.*, turpentine) to form the unstable peroxide. In some cases these unstable peroxides have been isolated. The bleaching and disinfecting properties of turpentine are due to its ability to activate oxygen in this way.

EXERCISES ON CHAPTER XIX

1. How is hydrogen peroxide prepared from (*a*) barium peroxide, (*b*) sodium peroxide ? What are the uses of hydrogen peroxide ?

2. In what way is pure hydrogen peroxide prepared ? Give its important properties.

3. Give examples of (*a*) the catalytic decomposition of hydrogen peroxide, (*b*) oxidising actions of hydrogen peroxide, (*c*) reducing actions of hydrogen peroxide.

4. What are the tests for hydrogen peroxide ? How is the substance estimated ?

5. Five c.c. of a solution of hydrogen peroxide are acidified with sulphuric acid, and shaken with manganese dioxide. 48·3 c.c. of oxygen (measured at S.T.P.) are evolved. How many grams of H_2O_2 does 1 litre of the solution contain ?

6. How has the formula of hydrogen peroxide been established ? Explain the difference in constitution between barium peroxide and lead peroxide. What experimental evidence is there in support of the constitutional formulæ attributed to these substances ?

7. What is meant by autoxidation ? Describe two experiments to illustrate this process. How is it explained ?

CHAPTER XX

CHEMICAL EQUILIBRIUM, AND THE LAW OF MASS-ACTION

Chemical affinity.—In the preceding chapters chemical reactions of various kinds have been considered, without any reference to the possible **cause of chemical change.** In the earlier history of chemistry it seems to have been assumed that substances which were closely related to one another (*e.g.*, mercury and gold) showed the greatest tendency to combine, hence the name **affinity** (from *affinis*, related) was given to the cause of chemical combination. When the mutual action of acids and alkalies was examined, it became clear that it is, on the contrary, *dissimilar* substances which enter most easily into combination, and in the electrochemical theory of Berzelius, in which substances of opposite electrochemical character were regarded as most prone to combination, the antithesis of the older idea found its sharpest expression.

It was assumed by the alchemists (with the exception of Van Helmont) that substances were destroyed on combination, so that an acid and alkali, for instance, had nothing in common with the salt produced from them. Boyle, in his "Sceptical Chymist" (1661), however, remarks that: "gold may be so altered, as to help to constitute several bodies, different from itself, and the other ingredients; yet it may be reduced again into the same yellow, fixed, ponderable, and malleable gold it was, before its mixture with them." He also observes that: "notwithstanding, the particles of some bodies are so closely united, yet there are some which may meet with particles of other denomination, which are disposed to be more closely united with some of them than they are amongst themselves." In this the *elective* character of chemical affinity is clearly expressed. Mayow (1674) also held very clear views on chemical affinity. If ammonia, he says, be added to hydrochloric acid, sal-ammoniac is produced, in which, it is true, neither acid nor alkaline properties are apparent. But if this is heated with potash, the ammonia is displaced, "because the acid is capable of entering into closer union" with potash than with ammonia. To show that an acid is not destroyed on neutralisation, he refers to the distillation of nitre with sulphuric acid, which displaces the nitric acid, and leaves in the retort the same substance as is produced by the direct action of sulphuric acid on potash. Nitre, on heating alone, does not lose nitric acid, because the acid is kept down by the attraction of the potash; if sulphuric acid is added, the nitric acid comes off, "because the volatile acid . . . has been expelled from the society of the alkaline salt by the more fixed vitriolic acid." Mayow gives a number of examples of this kind.

Similar views were held by Newton, who pointed out that potash becomes moist in the air, whilst nitre remains dry, in consequence of an **attraction** for moisture shown by the first substance, but not by the second. Similarly, mercury precipitates silver from its solution in nitric acid, copper in turn precipitates mercury, and iron precipitates copper, because of the increasing attractions of these metals for the acid. He suggested that the attractions might be electrical in character. There is still very little known of affinity, but it appears that Newton's speculation may be true.

Geoffroy (1718), and Bergman (1775), generalised the results, and stated that of three substances, A, B, and C, if A has a stronger attraction for B than C has, then A is able to decompose BC *completely*, turning out C and forming AB. Tables of affinity were therefore drawn up, giving the order in which acids, for instance, displaced each other both in solution and in the state of fusion.

Bergman's theory of elective affinities was called into question by Berthollet ("Researches into the Laws of Affinity," Cairo, 1799). He pointed out that the reaction $A + BC = AB + C$ does not always proceed to completion in one direction, as it should according to Bergman's theory. It may proceed in the opposite direction under different conditions, and in general is not complete: "in opposing the body A to the combination BC, the combination AC can never take place [completely], but the body C will be divided between the bodies A and B proportionally to the affinity and the quantity of each."

A chemical reaction, *e.g.*, $A + BC = AB + C$, may proceed only to a certain point, because the **opposed reaction**: $AB + C = A + BC$ can often take place under the *same* conditions, and at the same time as the direct reaction. A **state of equilibrium** is then reached, when the two opposing reactions **balance** each other, *i.e.*, proceed with equal speeds. This is denoted by: $A + BC \rightleftharpoons AB + C$.

Many examples of such states have already been given. Thus, steam is reduced by heated iron, giving hydrogen and oxide of iron: $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$ (p. 183). But *under the same conditions*, oxide of iron is reduced by hydrogen, giving iron and steam: $Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$. The oxygen is shared between the iron and the hydrogen, and a state of equilibrium is set up when the two reactions are balanced, *i.e.*, as much steam is decomposed as is produced, in a given time: $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$. Other examples are the decomposition of barium peroxide by heat (p. 168): $2BaO_2 \rightleftharpoons 2BaO + O_2$; and the dissociation of steam at high temperatures (p. 212): $2H_2O \rightleftharpoons 2H_2 + O_2$. Such reactions as the above, which can proceed in either direction, are called **reversible reactions.**

EXPT. 138.—Pour concentrated hydrochloric acid over crystals of Glauber's salt ($Na_2SO_4,10H_2O$). Filter off the white residue, wash with a little water, dry on a porous plate, and heat with concentrated sulphuric acid: fumes of hydrochloric acid are evolved, hence the precipitate is sodium chloride. The two reactions are: (1) $Na_2SO_4 + 2HCl \rightarrow 2NaCl + H_2SO_4$; (2) $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$. They are the two **component reactions** of the **reversible reaction**: $2NaCl + H_2SO_4 \rightleftharpoons Na_2SO_4 + 2HCl$. Commercial **saltcake** (p. 238) always contains traces of undecomposed salt and free sulphuric acid together, because, even at a red heat, the decomposition of salt by sulphuric acid is never complete.

Reversible and irreversible reactions.—There are a large number of chemical reactions which appear to be irreversible under all known conditions. Thus, magnesium burns in oxygen to form magnesium oxide: $2Mg + O_2 \rightarrow 2MgO$, and even at the highest temperatures this oxide appears to be stable. The oxidation of mercury, as in Lavoisier's experiment (p. 47), is a similar reaction, but is reversible: $2Hg + O_2 \rightleftharpoons 2HgO$. Again, all organic compounds burn in oxygen to produce carbon dioxide and water (if they contain only carbon, hydrogen, and possibly oxygen). Thus, sugar burns in this way: $C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$. There is no trace of sugar left in equilibrium with CO_2, H_2O, and O_2, and the reaction is irreversible. Nevertheless, the reverse reaction takes place in green plants under the influence of sunlight.

These examples show that very general statements, to the effect that *all* reactions are really reversible, must be accepted with reserve. Many apparently irreversible, and to all intents *complete*, reactions are, however, not so in reality. Thus, barium chloride solution is not completely, although it is very nearly completely, precipitated by sulphuric acid. In such cases the upper arrow will be written to show which reaction occurs to the larger extent: $BaCl_2 + H_2SO_4 \rightleftharpoons BaSO_4 + 2HCl$. Dulong found that if barium sulphate is boiled with successive quantities of potassium carbonate solution it is completely converted into barium carbonate; whilst barium carbonate, when boiled with successive quantities of potassium sulphate solution, is entirely transformed into barium sulphate: the reaction is therefore reversible; $BaSO_4 + K_2CO_3 \rightleftharpoons BaCO_3 + K_2SO_4$. Both $BaSO_4$ and $BaCO_3$ are commonly supposed to be "insoluble"; they are, however, very slightly soluble (*cf.* p. 103), and the reactions go on *in solution.* The solids, as such, do not in this case enter into reaction (*cf.* p. 168).

The equilibrium state.—If a state of equilibrium is reached, as a result of the balancing of two opposing reactions, it is the same no matter which of the two groups of substances, separated by the sign $\rightleftharpoons$, we bring together in the first instance. Thus, the same state of equilibrium is reached on heating hydrogen iodide to 444° for a sufficient time as is attained on heating a mixture of hydrogen and iodine vapour, in equivalent proportions, at the same temperature, $H_2 + I_2 \rightleftharpoons 2HI$. This is shown in Fig. 188. The curve *AC* represents the amounts of hydrogen iodide left after various times when that gas is heated; the curve *BC* represents the amounts of hydrogen iodide formed from hydrogen and iodine. The former diminish, owing to the reaction: $2HI \rightarrow H_2 + I_2$; the latter increase, owing to the reverse reaction: $H_2 + I_2 \rightarrow 2HI$. Both curves gradually coalesce to a horizontal line, *CD*, where equilibrium is reached. No further change then occurs: $H_2 + I_2 \rightleftharpoons 2HI$. **Equilibrium is a state which is independent of time.** This example shows that both reactions can go on under the same conditions; in the equilibrium state we assume that both are still proceeding, but the amount of hydrogen iodide formed in any instant of time is exactly equal to the amount which is decomposed. The two reactions are balanced, and a state of **kinetic equilibrium** is attained, not static, when all reaction ceases.

dynamic equil.

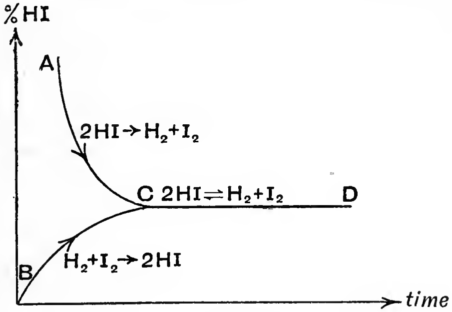


FIG. 188.—Curves illustrating attainment of Equilibrium State.

Kinetic theory of equilibrium.—The conception of the equilibrium state as the balance of two opposing reactions follows directly from the kinetic theory. Thus, a liquid comes into equilibrium with its vapour when as many molecules leap out of the liquid as return to it in a given interval (p. 270). A salt is in equilibrium with its saturated solution when as many molecules break away from the solid per second as are caught up again, possibly in a different part of the crystal (p. 272). If barium peroxide is heated in a closed vessel at a constant temperature, it breaks up into baryta and oxygen: $2BaO_2 \rightarrow 2BaO + O_2$. The oxygen molecules, by collision with the baryta, reproduce molecules of barium peroxide. The higher the pressure of the oxygen, the more frequent are the collisions of oxygen molecules on the baryta, and the greater is the rate of recombination.

The rate at which the peroxide molecules are breaking up is constant at a given temperature, hence at a certain pressure of oxygen the rate at which peroxide is reproduced becomes equal to the rate at which it is decomposed. A state of equilibrium is therefore set up at a definite pressure of oxygen, called the **dissociation pressure**: $2BaO_2 \rightleftharpoons 2BaO + O_2$. If the pressure of the oxygen is raised, the collisions become more frequent, additional combination takes place, and if the pressure is *maintained* above the dissociation pressure, all the oxygen is reabsorbed by the baryta. If the pressure of the oxygen is decreased, more peroxide decomposes, since less oxygen returns to it by collisions, and if gas is *continuously* pumped off, all the peroxide is ultimately decomposed. (The **Brin process,** p. 168.)

Effect of volatility or insolubility of a product of reaction.—In many cases a reaction appears to go to completion, instead of to a state of equilibrium. Berthollet remarked that this often results from some **disturbance of the equilibrium state,** by one or more of the products of the reaction being removed from the sphere of action by their **volatility,** or **insolubility.** As soon as they leave the system, passing into the gaseous state, or depositing as solids, they cease to exert any influence, and the reaction by which they are produced, being no longer opposed, cannot become balanced, and proceeds until the change becomes nearly, if not quite, complete.

Thus, if sulphuric acid is poured over common salt, a state of equilibrium is momentarily set up: $NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl \uparrow$. The hydrochloric acid, however, escapes from the liquid as a gas (shown by the upward-pointing arrow), the state of equilibrium is disturbed, and the reaction proceeds. When the decomposition has reached the stage where the hydrochloric acid remaining is only sufficient to saturate the liquid, evolution of gas ceases, but if the gas is partly expelled by heating, further reaction occurs. Decomposition is, however, never quite complete.

If sulphuric acid is added to barium chloride solution, double decomposition ensues: $BaCl_2 + H_2SO_4 \rightleftharpoons 2HCl + BaSO_4 \downarrow$. The barium sulphate, being very sparingly soluble, is precipitated (shown by the downward-pointing arrow); in this way it is removed from the sphere of action, and the reaction proceeds. The sulphate, however, is really very slightly soluble, so that when the amount dissolved is in equilibrium with the solid: $BaSO_4 \rightleftharpoons BaSO_4$ (dissd.), a state of equilibrium is set up. The four substances are then in solution: $BaCl_2 + H_2SO_4 \rightleftharpoons 2HCl + BaSO_4$ (dissd.) $\rightleftharpoons BaSO_4$ (ppd.).

Investigation of equilibrium states.—The preceding examples show that if a state of equilibrium has been set up, it may be disturbed by withdrawing one or more of the interacting substances from the sphere of action. In examining the proportions of the substances existing in equilibrium, it is also necessary to ensure that the reverse reaction does not take place when the conditions are changed. Thus, if hydrogen iodide is heated until equilibrium is attained: $2HI \rightleftharpoons H_2 + I_2$, the proportions of HI, H_2, and I_2 may be determined by rapidly cooling the mixture, when very little reaction occurs (p. 351). In some cases, *e.g.*, the dissociation of steam: $2H_2O \rightleftharpoons 2H_2 + O_2$, this cooling must be performed exceedingly quickly, otherwise the reverse reaction occurs, and no trace of the products of dissociation can be discovered.

Dissociation.—The investigation of states of equilibrium attained in the dissociation of substances by heat illustrates the point to which reference has just been made.

Grove (1847) heated a platinum wire in steam by an electric current. In contact with the hot wire, dissociation occurred and the products at once passed into the diluting atmosphere of steam, which prevented their recombination by separating them and by cooling. If a heated platinum wire (the temperature of which can be measured from its electrical resistance) is allowed to remain for a sufficient length of time in a flask of steam, the products of dissociation and the unchanged steam are continually brought in contact with the heated wire by diffusion, and a state of equilibrium is ultimately attained, corresponding with the temperature of the wire.

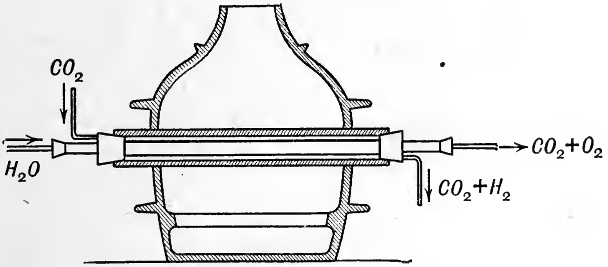


FIG. 189.—Deville's Experiment on Dissociation.

Deville (1864) demonstrated the dissociation of gases at high temperatures by means of the apparatus shown in Fig. 189. A wide tube of glazed porcelain, with a narrower tube of unglazed porcelain supported axially inside, was heated strongly in a furnace. Water vapour was passed through the inner tube, and carbon dioxide through the annular space, and the gases from both were collected over potash solution, which absorbed the carbon dioxide. The steam was dissociated, and the hydrogen passed out by diffusion through the porous tube into the annular space, leaving most of the oxygen in the inner tube. If the two gases were passed to the same receiver, 1 c.c. of detonating gas ($2H_2 + O_2$) was collected for every gram of water passed through the apparatus. If carbon dioxide was passed rapidly through a glazed porcelain tube packed with fragments of porcelain heated in a furnace to 1200–1300°, dissociation occurred : $2CO_2 \rightleftharpoons 2CO + O_2$. When the gas was collected over caustic potash, a mixture of carbon monoxide and oxygen was obtained.

The effect of concentration. The law of "mass-action."—Berthollet, in addition to his proof of the reversibility of reactions, made the important discovery that the extent of reaction depends on the quantity of reacting substance present in a given volume, or its **concentration.** The **activity** of a substance, as he says (p. 345), is "proportional to the affinity and the *quantity*" ; by "quantity" he meant "concentration." The activity is therefore proportional to the product : **(affinity)** × **(concentration)**, which Berthollet called the **active mass.** A weak affinity could thus be compensated by a large concentration, and a strong affinity weakened by high dilution.

A substance, B, may be shared between two others, A and C, to form AB and BC : $A + BC \rightleftharpoons$ ~~$AC + B$.~~ $AB + C$ If the amount of A is increased, more of B goes to A, and a new state of equilibrium is set up, in which the ratio AB/BC is greater than before. Although the actual affinities of A and C for B remain unchanged, that of A appears to have increased, because the effect of A is proportional not only to its affinity, but also to its concentration ; in other words, to the product of affinity and concentration, which is called the **active mass.**

Thus, **in reversible reactions, the extent of chemical change is proportional to the active masses of the interacting substances.** If to a system of substances in equilibrium an excess of one reacting substance is added, change occurs in such a way that the concentration of that substance is diminished. This is known as **the law of mass-action.**

The law may be illustrated by an experiment due to J. H. Gladstone (1855). Ferric chloride and potassium (or ammonium) thiocyanate react in solution to produce ferric thiocyanate, which has a blood-red colour. The reaction is reversible : $FeCl_3 + 3KCNS \rightleftharpoons Fe(CNS)_3 + 3KCl$, and if an excess of $FeCl_3$ or KCNS is added, the intensity of the colour deepens. But if KCl is added, the reverse reaction is favoured by the action of mass, and the colour becomes paler.

EXPT. 139.—Prepare two solutions containing 2·7 gm. of crystallised ferric chloride ($FeCl_3,6H_2O$), and 23 gm. of $NH_4{\cdot}CNS$, in 1 litre of water, respectively. Mix 100 c.c. of each. A dark red solution of $Fe(CNS)_3$ is formed. Add 25 c.c. of this solution to 1 litre of water in each of four glass cylinders ; a pale brownish-red colour is produced. Keep one jar for reference, and to the other three add : (*a*) 25 c.c. of the ferric chloride solution; (*b*) 25 c.c. of the thiocyanate solution; (*c*) 25 c.c. of a saturated solution of NH_4Cl. Observe and explain the colour change in each case.

The **concentration** of a substance is usually measured by **the number of gram molecules per litre.** Thus, if a gas mixture contains 3·62 gm. of HCl per litre, the concentration is 0·1. Similarly, a solution of 97 gm. of KCNS per litre has a concentration of 1. It is convenient to denote the concentration of a substance by its chemical symbol enclosed in square brackets, *e.g.*, [KCNS] = 1 means 97 gm. of KCNS, or the amount represented by the formula, in 1 litre.

Velocity of reaction.—The usual method of determining the activity of a substance is the measurement of the rate at which a chemical reaction involving that substance proceeds, and the effect of change of concentration of the substance on this rate, or **velocity, of reaction.**

Thus, the rate of combination of hydrogen and iodine vapour, at a fixed temperature (*e.g.*, 444°): $H_2 + I_2 \rightarrow 2HI$, may be measured by taking a number of bulbs containing the two substances, heating them all to 444°, cooling successive bulbs after different intervals of time, and determining the amount of unchanged hydrogen by opening the bulb under potassium iodide solution. If a c.c. of hydrogen was taken initially, and $(a-x)$ c.c. is left after an interval of time t, the amount of hydrogen which has taken part in the reaction is x c.c.

In the same way, by starting with pure hydrogen iodide, and measuring the volumes of hydrogen produced after different intervals of time, we can find the rate of decomposition of HI.

Since we assume the velocity of reaction to be proportional to the activity of a substance, and the latter, at a fixed temperature, is proportional to the concentration, it follows that the rate of combination of hydrogen and iodine vapour, *i.e.*, the number of molecules of H_2 or I_2 combining in unit time, will be proportional to the concentration of each, *i.e.*, proportional to the product of the concentrations:

$$\textbf{Rate of combination of } \mathbf{H_2} \textbf{ and } \mathbf{I_2} = \mathbf{k_1 [H_2] \times [I_2]} \quad . \quad . \quad . \quad . \quad (1)$$

The constant k_1 is called the **velocity constant**: it is the rate of combination when $[H_2] = [I_2] = 1$, *i.e.*, when the concentrations are unity.

In the same way, the rate of decomposition of hydrogen iodide is proportional to the active masses. Now *two* molecules of HI are decomposed: $HI + HI \rightarrow H_2 + I_2$, hence:

$$\textbf{Rate of decomposition of HI} = \mathbf{k_2 [HI]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The two reactions: (*a*) $H_2 + I_2 \rightarrow 2HI$, (*b*) $2HI \rightarrow H_2 + I_2$, go on simultaneously; hence, since HI is at the same time being formed and decomposed:

Rate of formation of HI = Rate of combination of H_2 and I_2 to HI
— Rate of decomposition of HI
= $k_1 [H_2] \times [I_2] - k_2 [HI]^2$.

This may be positive, negative, or zero, according to the values of $k_1 [H_2] \times [I_2]$ and $k_2 [HI]^2$. When the rate of formation of HI is zero the system is in **equilibrium,** since then HI is decomposed exactly as fast as it is formed, so that the amount of HI is independent of the time. Hence **in equilibrium:**

$$k_1 [H_2] \times [I_2] - k_2 [HI]^2 = 0.$$

$$\therefore \quad \mathbf{k_1 [H_2] [I_2] = k_2 [HI]^2}$$

$$\text{or} \quad \frac{[H_2]\,[I_2]}{[HI]^2} = \frac{k_2}{k_1} = K \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

At a given temperature, K is constant: it is called the **equilibrium constant.** It is independent of the amounts of iodine, hydrogen, and hydrogen iodide originally taken, but depends on the temperature. Equation (3) is the quantitative expression of the **law of mass-action** for the case under consideration. The quantitative expression of the law is due to Guldberg and Waage (1864).

The **general equation of mass-action** can now be written down. Let the reaction:

$$A + B + C + \ldots \rightleftharpoons A' + B' + C' + \ldots$$

occur, and let it be **reversible.** *E.g.*, the reaction may be:

$$H_2 + I_2 \rightleftharpoons HI + HI$$

$$\text{or} \quad H_2 + H_2 + O_2 \rightleftharpoons H_2O + H_2O,$$

each interacting molecule being written separately. Then the **velocity of reaction** is:

$$k_1 [A] [B] [C] \ldots - k_2 [A'] [B'] [C'] \ldots$$

where $[A]$, etc., are the **concentrations** in gm. mols. per litre, and k_1, k_2 are the **velocity constants.** In **equilibrium** the velocity is zero, hence:

$$\frac{[A'] [B'] [C'] \ldots}{[A] [B] [C] \ldots} = k_1/k_2 = K$$

where K is the **equilibrium constant.**

We shall always write the product of the concentrations of the **products** of the reaction in the numerator, and the product of the concentrations of the **initial substances** in the denominator; the larger the value of K, therefore, the greater will have been the extent of the forward reaction when equilibrium is attained.

Thus, if we consider the reaction : $3NH_4 \cdot CNS + FeCl_3 \rightleftharpoons Fe(CNS)_3 + 3NH_4Cl$, we shall have the equilibrium equation :

$$\frac{[Fe(CNS)_3]\ [NH_4Cl]^3}{[FeCl_3][NH_4CNS]^3} = K.$$

Addition of NH_4CNS or NH_4Cl will therefore displace the equilibrium to a much greater extent than addition of the equimolecular amount of $FeCl_3$ or $Fe(CNS)_3$, because the *cubes* of the concentrations of the former substances are involved.

If a reaction is **irreversible,** there is no back-reaction, and the speed is simply : $k_1 [A] [B] [C] \ldots$ There cannot be equilibrium unless one of the concentrations is equal to zero, *i.e.*, *the reaction is complete.* This agrees with what has been said of such reactions ; they proceed to completion, without any measurable state of equilibrium being set up.

If the reaction is reversible, the velocity constant k_1 may sometimes be measured at the beginning of the reaction, before the products have accumulated in quantities sufficient to set up an appreciable back-reaction. In other cases the velocity constant can be calculated by methods which cannot be described here. (See the author's " Higher Mathematics for Chemical Students." Methuen.)

Kinetic derivation of the law of mass-action.—We have so far considered the law of mass-action as an **experimental fact.** It may, however, be deduced : (1) from thermodynamics ; (2) from the kinetic molecular theory. A sketch of the second method, due to Guldberg and Waage, will be given here.

Consider the formation of hydrogen iodide from hydrogen and iodine. Molecules of HI can only be formed as the result of **collisions** of iodine and hydrogen molecules in the gas, the number of collisions per second being proportional to the number of molecules of each gas present in unit volume, *i.e.*, to their concentrations. It is therefore proportional to the product of these concentrations, $k [H_2] \times [I_2]$. It may not be every collision which results in the formation of hydrogen iodide, but we can assume that a definite fraction x of the total number of collisions will be effective ; hence the speed is equal to $xk [H_2] [I_2]$, or $k_1 [H_2] [I_2]$ where $k_1 = xk$, and x, k, are constants. Similarly, the speed of the reverse reaction will be $k_2 [HI]^2$, since *two* HI molecules must collide, and the probability for this is proportional to $[HI]^2$.

Those molecules which are in a condition to undergo chemical change on collision (**active molecules**) appear to be those possessing more than a certain critical amount of **internal energy,** due to atomic rotation or vibration. When a molecule acquires this **critical increment** of internal energy it becomes active

Thermal dissociation.—Let 2 gm. mol. (254 gm.) of hydrogen iodide gas, contained in a sealed bulb of volume V litres, be heated at 444° in the vapour of boiling sulphur. After a certain lapse of time a state of **equilibrium** is attained :

$$HI + HI \rightleftharpoons H_2 + I_2.$$

Let the fraction γ of the hydrogen iodide be dissociated; the equilibrium concentrations will then be as follows :

$$\begin{array}{cccc} HI + & HI \rightleftharpoons & H_2 + & I_2 \\ [HI] & [HI] & [H_2] & [I_2] \\ \dfrac{1-\gamma}{V} & \dfrac{1-\gamma}{V} & \dfrac{\gamma}{V} & \dfrac{\gamma}{V} \end{array}$$

The law of mass-action states that the product of the concentrations of the substances formed in the reaction, divided by the product of the concentrations of the original substances which remain, is equal to a constant, K, at a given temperature :

$$\frac{[I_2] \times [H_2]}{[HI] \times [HI]} = \frac{\dfrac{\gamma}{V} \cdot \dfrac{\gamma}{V}}{\dfrac{1-\gamma}{V} \cdot \dfrac{1-\gamma}{V}} = \frac{\gamma^2}{(1-\gamma)^2} = K \quad . \quad . \quad . \quad . \quad (1)$$

The resulting equation does not contain V, so that the degree of dissociation γ, of HI, is independent of the volume of the bulb in which the HI was initially confined ; in other words, it is *independent of the pressure,* and depends only on the temperature.

Example.—7 94 c.c. of hydrogen (at S.T.P.) and 0·0601 gm. of solid iodine were heated in a sealed bulb at 444° until equilibrium was reached. 9·52 c.c. of hydrogen iodide were formed. Now at S.T.P. 2 × 126 gm. of iodine (I_2) occupy 22,240 c.c.

∴ vol. of I_2 vapour at S.T.P. initially present

$$= \frac{22240 \times 0{\cdot}0601}{2 \times 126} = 5{\cdot}30 \text{ c.c.}$$

Each c.c. of HI formed diminishes the volume of the H_2 and I_2 by 0·5 c.c. each, ∴ in equilibrium :

vol. of $H_2 = 7{\cdot}94 - 4{\cdot}76 = 3{\cdot}18$ c.c. $(4{\cdot}76 = 0{\cdot}5 \times$ vol. of HI $= 0{\cdot}5 \times 9{\cdot}52)$

vol. of $I_2 = 5{\cdot}30 - 4{\cdot}76 = 0{\cdot}54$ c.c.

vol. of HI $= 9{\cdot}52$. Hence, if V is the volume of the bulb, the **concentrations** are: $[H_2] = 3{\cdot}18/22240V$; $[I_2] = 0{\cdot}54/22240V$; $[HI] = 4.76/22240V$.

Hence : $$K = \frac{[H_2] \times [I_2]}{[HI]^2} = \frac{3{\cdot}18 \times 0{\cdot}54}{(4{\cdot}76)^2} = 0{\cdot}0758.$$

Now, suppose 8·10 c.c. of hydrogen and 2·94 c.c. of iodine vapour (at S.T.P.) heated to 444°. What volume of HI will be formed in equilibrium? Let $2x$ c.c. be formed:

$$\begin{array}{lcccc} & H_2 & + \quad I_2 & \rightleftharpoons & HI + HI \\ \text{Volumes:} & (8\cdot10 - x) & (2\cdot94 - x) & & x \qquad x \end{array}$$

$$\therefore \frac{(8\cdot10 - x)(2\cdot94 - x)}{x^2} = 0\cdot0758$$

$\therefore x = 2\cdot822$ or $9\cdot12$. Only the root 2·82 is admissible, since 2·94 c.c. I_2 vapour can give only 5·88 c.c. HI as a maximum. Thus, volume of HI formed = 2 × 2·82 c.c. = **5·64 c.c.** Bodenstein by experiment found 5·66 c.c.

Effect of temperature and pressure on equilibrium.—The dissociation of hydrogen iodide cannot be measured by the **change of density,** because the volume is unchanged. But if an increase of volume occurs, the extent of dissociation can be measured, as described on p. 152, from the vapour density. This is the case with **phosphorus pentachloride:**

$$\begin{array}{lccccc} & PCl_5 & \rightleftharpoons & PCl_3 & + & Cl_2 \\ \text{Concentrations:} & \frac{1-\gamma}{V} & & \frac{\gamma}{V} & & \frac{\gamma}{V} \end{array}$$

$$\therefore \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\gamma^2}{(1-\gamma)V} = K.$$

The extent of dissociation now *depends on the volume*, V, and therefore on the *pressure*, which was not the case with HI, since in the latter case V cancelled out in the equilibrium equation.

If V is increased (*i.e.*, the pressure diminished), the denominator in the above expression for K becomes too large; the numerator, and therefore γ, must also increase in order to maintain the value of the equilibrium constant. Hence the extent of dissociation increases, in this reaction, when the pressure is reduced. The same effect is produced by adding an indifferent gas, which reduces the partial pressures. A change of volume or pressure influences the state of equilibrium only when the chemical reaction causes a change of volume (*e.g.*, PCl_5 (1 vol.) = $PCl_3 + Cl_2$ (2 vols.)). If no change of volume occurs (*e.g.*, $2HI = H_2 + I_2$), pressure has no influence on the equilibrium. If the pressure on a system in equilibrium is increased, that change occurs which leads to a diminution of volume, *i.e.*, a decrease of pressure, and the equilibrium is correspondingly shifted. This is a special case of the **law of reaction**: *if a system in equilibrium is subjected to a constraint, a change occurs, if possible, of such a kind that the constraint is partially annulled.* The **effect of pressure on equilibrium** is so regulated.

Another aspect of this law is the **effect of temperature on equili-**

brium. If the temperature of the system in equilibrium is raised (or lowered), that one of the two reversible reactions will occur which absorbs (or evolves) heat. Thus, the dissociation of PCl_5 is increased by raising the temperature, because the reaction $PCl_5 = PCl_3 + Cl_2$ occurs with absorption of heat.

If Q_v is the **heat of reaction** at constant volume (p. 387), and K_1, K_2 are the equilibrium constants corresponding with the absolute temperatures T_1 and T_2, then it is shown by thermodynamics that, if 1 gm. molecule of substance is taken :

$$\log K_2 - \log K_1 = \frac{Q_v}{4{\cdot}571}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

In this way the heat of reaction may be calculated.

EXAMPLE.—2·0 gm. of PCl_5 are sealed in an evacuated bulb of 200 c.c. capacity, heated to 200°. Find the pressure developed if PCl_5 is 48·5 per cent. dissociated under 1 atm. pressure.

2·0 gm. of $PCl_5 = 2{\cdot}0/207 = 0{\cdot}0097$ gm. mol. Let x = degree of dissociation under conditions of experiment. Let the volumes be measured in litres ; then

$$[PCl_5] = \frac{0{\cdot}0097 - x}{0{\cdot}20};\ [PCl_3] = [Cl_2] = \frac{x}{0{\cdot}20}\ \therefore\ K = \frac{x^2}{(0{\cdot}0097 - x) \times 0{\cdot}2}.$$

But at 200° under 1 atm. pressure PCl_5 is 48·5 per cent. dissociated. The volume of 1 gm. molecule under these conditions is

$$22{\cdot}24 \times 1{\cdot}485 \times \frac{473}{273} = 57{\cdot}2 \text{ lit.}$$

$$\therefore K = \frac{(0{\cdot}485)^2}{0{\cdot}515 \times 57{\cdot}2} = 0{\cdot}007984. \quad \text{Hence } \frac{x^2}{(0{\cdot}0097 - x) \times 0{\cdot}2} = 0{\cdot}007984$$

$\therefore\ x = \mathbf{0{\cdot}0033}$. There are thus $1{\cdot}0033 \times 0{\cdot}0097$ gm. mol in 200 c.c.

$$\therefore \text{ pressure} = 1{\cdot}00973 \times \frac{473}{273} \times \frac{22{\cdot}24}{0{\cdot}2} = \mathbf{1{\cdot}93 \text{ atm.}}$$

(If the pressure is doubled, the dissociation diminishes from 48·5 to 0·33 per cent.)

Effect of addition of products of dissociation.—Let 2 gm. mol. of hydrogen iodide, contained in a volume V, be dissociated to the extent γ. Now suppose x gm. mol. of hydrogen (or iodine vapour) introduced into the vessel, at the same temperature. The original concentrations (see p. 354) were : $[HI] = (1 - \gamma)/V$; $[H_2] = \gamma/V$; $[I_2] = \gamma/V$, and $\gamma^2/(1 - \gamma)^2 = K$. When the excess of hydrogen is added, $[H_2] = (\gamma + x)/V$. The product is now $\gamma(\gamma + x)/(1 - \gamma)^2$, which is greater than K. Hence γ must *diminish* to a value γ', such that $\gamma'(\gamma' + x)/(1 - \gamma')^2 = K$. The extent of dissociation is therefore diminished by adding hydrogen or iodine vapour *at constant volume*.

Now suppose a volume nV of hydrogen (or iodine vapour) added,

[illegible]

at the same concentration as it exists in the mixture, i.e., V contains γ gm. mol. The concentrations are now :

$[HI] = (1 - \gamma)/(1 + n)V$; $[H_2] = \gamma(1 + n)/V(1 + n) = \gamma/V$; $[I_2] = \gamma/V(1 + n)$.

The product is $(1 + n)\gamma^2/(1 - \gamma)V$, which is greater than K. The value of γ must therefore diminish, *i.e.*, the dissociation is diminished, although the volume is increased.

In the case of the dissociation of PCl_5, the addition of x gm. mol. of PCl_3 (or Cl_2) at *constant volume* changes the concentrations in the mixture to: $[PCl_5] = (1 - \gamma)/V$; $[PCl_3] = (\gamma + x)/V$; $[Cl_2] = \gamma/V$. Their product is: $(\gamma + x)\gamma/(1 - \gamma)V$, which is larger than the equilibrium value. The extent of dissociation, γ, must therefore diminish on adding one of the products of dissociation when the volume is constant.

But if nV volumes of PCl_3 (or Cl_2) are added *at the same concentration as it exists in the mixture, i.e., V* volumes contain γ gm. mol., then the concentrations are :

$[PCl_5] = (1 - \gamma)/V(1 + n)$; $[PCl_3] = \gamma(1 + n)/V(1 + n)$; $[Cl_2] = \gamma/V(1 + n)$,

and their product is $\gamma^2/(1 - \gamma)V$, *i.e.*, K, so that *no change is produced*.

Since there are now $1 + \gamma(1 + n)$ molecules in a volume $V(1 + n)$, whereas before the addition of PCl_3 or Cl_2 there were $1 + \gamma$ molecules in a volume V, *i.e.*, $(1 + \gamma)(1 + n)$, or $1 + \gamma(1 + n) + n$, molecules in a volume $V(1 + n)$, it follows that the total pressure is reduced by addition of a product of the dissociation at the same *partial* pressure as it exists in the mixture. If this substance is added so that the *total* pressure remains constant, it follows that the dissociation will be reduced. This was shown by Wurtz (1873) : if PCl_5 is volatilised into an atmosphere of PCl_3 at atmospheric pressure, the dissociation is largely suppressed, and only a very pale greenish colour, due to chlorine, is seen.

Electrolytic dissociation.—If a salt, acid, or base is dissolved in water, its molecules are partially broken up into ions, the **degree of ionisation,** α, increasing with dilution to a limiting value 1, when dissociation is complete : $NaCl \rightleftharpoons Na^{\cdot} + Cl'$. Let 1 gm. mol. of electrolyte be dissolved in a volume V. The concentrations are then :

$$[NaCl] = (1 - \alpha)/V ; \quad [Na^{\cdot}] = [Cl'] = \alpha/V.$$

If the law of mass-action applies to ionisation we have :

$$\frac{[Na^{\cdot}][Cl']}{[NaCl]} = \frac{\alpha^2}{(1 - \alpha)V} = K.$$

This equation is known as **Ostwald's dilution law** (1886). It applies with very great exactness to **weak electrolytes,** as may be seen from the values of K, the **ionisation constant,** for acetic acid on p. 291. In the case of **strong electrolytes,** however, it fails completely, as may be seen from the values of K for potassium chloride on p. 291. The reason for the anomalous behaviour of strong electrolytes is not known.

Solubility product.—If solid sodium chloride is in contact with its saturated solution we have two connected equilibria :

$$\text{NaCl (solid)} \rightleftharpoons \text{NaCl (dissd.)} \rightleftharpoons \text{Na}^{\cdot} + \text{Cl}'.$$

The **total solubility** of sodium chloride is the sum of the amounts of the undissociated NaCl molecules (sometimes called the **true solubility**), and of the NaCl dissociated into ions, $Na^{\cdot}$ and Cl'.

If the law of mass-action applies to the ions (*cf.* above) we have : $[Na^{\cdot}] \times [Cl'] = K[NaCl]$. But [NaCl] is the concentration of un-ionised salt, *i.e.*, the true solubility. It is assumed that this is always constant at a given temperature, if excess of solid is present. Hence, in equilibrium, **the product of the ionic concentrations is constant** at a given temperature. This constant product, *e.g.*, $[Na^{\cdot}] \times [Cl']$, is called the **solubility product.** When the product of the ionic concentrations, or the **ionic product,** is *equal to* the solubility product, the solution is in *equilibrium* with the solid, since then the concentration of un-ionised salt in solution must be that which is in equilibrium with solid. If the ionic product is *less* than the solubility product, the solution is unsaturated with respect to the solid, and more of the latter dissolves. But if the ionic product is *greater* than the solubility product, the solution is supersaturated, and precipitation of solid usually occurs. In some cases the solution remains supersaturated.

The value of the ionic product may be increased by adding to the solution an electrolyte which has an ion in common with the substance in solution. Thus, if hydrochloric acid is added to a saturated solution of common salt, the concentration of chloride ions is increased, and the ionic product, $[Na^{\cdot}] \times [Cl'$ from NaCl + added Cl' from HCl$]$, is increased above the value corresponding with the solubility product. Solid sodium chloride is then precipitated until the ionic product becomes equal to the solubility product, *i.e.*, until the concentration of the un-ionised salt in solution is reduced to its original value, the true solubility. The other ion of the added electrolyte, $H^{\cdot}$, has no effect on the equilibrium, as may be proved by adding a quantity of another chloride, *e.g.*, LiCl, containing the same quantity of chloride ions as the acid, when the same weight of NaCl is precipitated as in the first experiment. If an equivalent amount of $Na^{\cdot}$ ions, *e.g.*, as $NaClO_3$, had been added instead of Cl' ions, the effect is exactly the same, as it should be, since the product $[Na^{\cdot}] \times [Cl']$ is affected to the same extent by equivalent amounts of $Na^{\cdot}$ and Cl'.

EXPT. 140.—Pass gaseous hydrochloric acid into a filtered saturated solution of common salt, which contains magnesium chloride as impurity, using the apparatus shown in Fig. 190 A white crystalline powder of NaCl falls. This is filtered off, washed with a little pure concentrated hydrochloric acid, and, after removing mother liquor in a Büchner funnel, is dried on a porous plate. The salt is heated carefully in a platinum dish to drive off HCl, and is then pure.

EXPT. 141.—To a saturated solution of silver acetate add: (*a*) a concentrated solution of silver nitrate: (*b*) a saturated solution of sodium acetate In each case silver acetate is precipitated.

EXPT. 142.—To a saturated solution of potassium perchlorate add: (*a*) perchloric acid; (*b*) a saturated solution of potassium chloride; (*c*) a saturated solution of sodium chloride; (*d*) concentrated hydrochloric acid. Explain the effect in each case. In case (*d*), if HCl is "hydrated" in solution, it would be expected to withdraw "free water" from the solution of the salt. From the result, consider whether this "explanation" covers EXPT. 140.

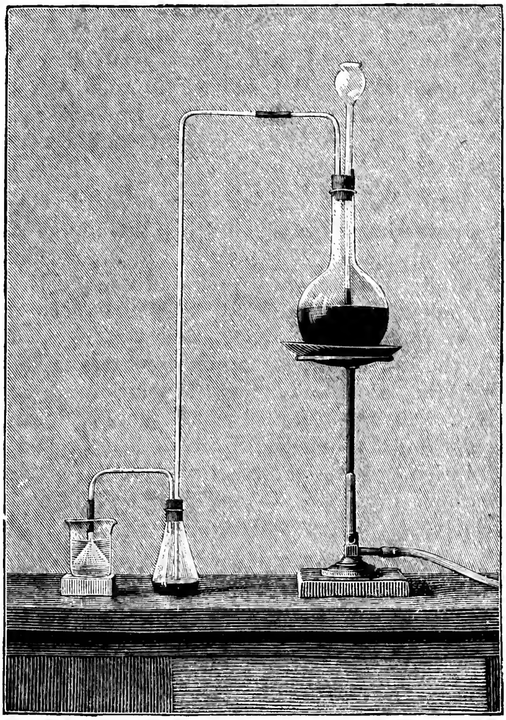


FIG. 190.—Preparation of Pure Sodium Chloride.

The effect of adding a **slight excess of a reagent** in analytical chemistry is now clear. If *exactly equivalent* amounts of silver nitrate and hydrochloric acid in aqueous solution are mixed, precipitation of silver chloride occurs: $Ag^{\cdot} + Cl' \rightleftharpoons AgCl \downarrow$. If the precipitate is filtered off, and either silver nitrate or hydrochloric acid added to the clear filtrate, an opalescence is produced, owing to precipitation of AgCl. A trace of the latter existed in solution, almost completely ionised at the great dilution, and when a common ion was added the ionic product, $[Ag^{\cdot}] \times [Cl']$, exceeded the solubility product. In the quantitative precipitation of silver, or of chlorides, a slight excess of a chloride, or of silver nitrate, respectively, is added. The precipitation is then practically complete.

If a *large* excess of concentrated hydrochloric acid is added to the precipitate of silver chloride, some of the latter dissolves. In this case, however, the substance in solution is not AgCl but a **complex substance,** probably H_2AgCl_3, which ionises as follows: $H_2AgCl_3 \rightleftharpoons 2H^{\cdot} + AgCl_3''$. The solution contains no silver ions, $Ag^{\cdot}$, and the phenomenon is not an exception to the solubility product equation. As a general rule, too great an excess of reagent should not be added in precipitation reactions.

Expt. 143.—To a solution of silver nitrate add drop by drop a solution of potassium cyanide, KCN. A white precipitate of silver cyanide is first produced: $Ag^{\cdot} + CN' \rightleftharpoons AgCN\downarrow$. On continued addition of the cyanide this precipitate redissolves, and the solution then contains the complex anion $Ag(CN)_2'$: $AgCN + CN' \rightleftharpoons Ag(CN)_2'$. There are then present $2K^{\cdot}$, NO_3', and $Ag(CN)_2'$, *i.e.*, KNO_3 and $KAg(CN)_2$. In the latter salt, **potassium argentocyanide,** the silver is present in the acid radical, or anion, and the solution is practically free from silver ions, $Ag^{\cdot}$. It gives, for instance, no precipitate of AgCl with a soluble chloride. Complex ions are slightly broken up into the simple ions in solution. Thus, the reaction $Ag(CN)_2' \rightleftharpoons Ag^{\cdot} + 2CN'$ occurs to a slight extent, and silver is deposited on the cathode from this solution in electroplating (p. 825).

Hydrolysis.—A number of salts are decomposed to a greater or less extent on solution in water, with the separation of acid and base. The reaction is known as **hydrolysis**.

Thus, a solution of potassium cyanide has an alkaline reaction, and smells of hydrocyanic acid, owing to hydrolysis: $KCN + H_2O \rightleftharpoons KOH + HCN$.

Expt. 144.—Heat about 5 gm. of plaster of Paris with half its weight of powdered charcoal in a covered crucible. Calcium sulphide is formed: $CaSO_4 + 4C = CaS + 4CO$. When cold, add the solid to water. The liquid will be found alkaline to litmus, and, on warming, sulphuretted hydrogen is evolved, turning lead acetate paper black: $CaS + 2H_2O \rightleftharpoons Ca(OH)_2 + H_2S$. H. Rose (1842) found that the hydrolysis in this case increases with the dilution.

Expt. 145.—To a *concentrated* solution of borax add silver nitrate. A white precipitate of silver metaborate is formed:

$$Na_2B_4O_7 + 3H_2O \rightleftharpoons 2NaBO_2 + 2H_3BO_3;$$
$$NaBO_2 + AgNO_3 = AgBO_2 + NaNO_3.$$

Repeat the experiment with a *very dilute* solution of borax: a brown precipitate of silver oxide is obtained:

$$NaBO_2 + 2H_2O \rightleftharpoons NaOH + H_3BO_3;$$
$$2NaOH + 2AgNO_3 = 2NaNO_3 + Ag_2O + H_2O.$$

In the above examples, the salts are formed from *a weak acid and a strong base.* *E.g.*, H_2S and $Ca(OH)_2$; H_3BO_3 and NaOH; HCN and NaOH (*cf.* p. 422). In solution, the weak acid is scarcely ionised at all, the slight ionisation which would occur in pure water being almost completely suppressed by the action of the anion, which is produced from the largely ionised salt: $HCN \rightleftharpoons H^{\cdot} + CN'$; $KCN \rightleftharpoons K^{\cdot} + CN'$. The strong base, on the other hand, is largely ionised: $KOH \rightleftharpoons K^{\cdot} + OH'$; so that the solution exhibits: (i) the properties of the free acid, (ii) a strongly alkaline reaction, due to hydroxide ions from the strong base.

With salts of a *strong acid and a weak base*, the results are the opposite of those just described.

Expt. 146.—Test with litmus paper solutions of copper sulphate and ferric chloride: notice the acid reaction.

Expt. 147.—Pour a dilute solution of ferric chloride on a parchment paper dialyser (p. 314), and float on water. The water becomes acid, hydrochloric acid diffusing through the membrane, and colloidal ferric hydroxide is left in the dialyser: $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$.

In a solution of ferric chloride, the ferric hydroxide, $Fe(OH)_3$, which exists in the state of a colloidal solution (*cf.* p. 989), is a very weak base, practically not ionised, whilst the hydrochloric acid is largely ionised. Hence the solution has an acid reaction, from the presence of hydrogen ions: $HCl \rightleftharpoons H^{\cdot} + Cl'$. The dark brown colour of the dialysed solution is due to the un-ionised base, $Fe(OH)_3$.

In a solution of a salt of *a weak acid with a weak base* hydrolysis also occurs. Thus, a solution of ammonium carbonate is alkaline, because, although ammonia is a weak base, it is stronger than carbonic acid: $(NH_4)_2CO_3 + 2H_2O \rightleftharpoons 2NH_4OH + H_2CO_3$; $NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'$; $H_2CO_3 \rightleftharpoons HCO_3' + H^{\cdot}$.

Very slight hydrolysis probably occurs in solutions of *all* salts: it may become appreciable at high temperatures.

Expt. 148.—Heat a little NaCl in a platinum crucible to redness, and add a few drops of water. These assume the spheroidal state. After a few seconds transfer the drop of water to a beaker containing distilled water faintly coloured with litmus: this is turned red. Allow the crucible to cool, dissolve the salt in water, and add to dilute red litmus solution: this is turned blue. $NaCl + H_2O \rightleftharpoons HCl + NaOH$.

The law of mass-action may be applied to hydrolytic reactions :

$$\frac{[\text{acid}] \times [\text{base}]}{[\text{salt}] \times [\text{water}]} = K.$$

Hydrolysis may be considered as due to the action of the **ions of water.** If sodium hypochlorite, for instance, is dissolved in water, it first of all ionises : this occurs to a considerable extent, since nearly all salts are largely ionised in solution (p. 294) : $NaOCl \rightleftharpoons Na^{\cdot} + OCl'$. The ion OCl' thus finds itself in the presence of a very small concentration of hydrogen ions derived from the ionisation of water. Combination then occurs between the OCl' ions and $H^{\cdot}$ ions to form undissociated HOCl, since the ionisation of this acid is so slight, especially in presence of the large number of OCl' ions, that *the concentration of* $H^{\cdot}$ *ions derived from it* : $HOCl \rightleftharpoons H^{\cdot} + OCl'$, *is less than the concentration of* $H^{\cdot}$ *ions derived from water* : $H_2O \rightleftharpoons H^{\cdot} + OH'$. By reason of the removal of $H^{\cdot}$ ions, further ionisation of water occurs, and the reaction $H^{\cdot} + OCl' \rightleftharpoons HOCl$ proceeds until the concentration of HOCl in the solution is such that the $H^{\cdot}$ ions formed by its excessively slight dissociation are in equilibrium with the OH' ions produced from the water : $[H^{\cdot}] \times [OH'] = [H_2O] = \text{const.}$ It is these OH' ions which give the solution its alkaline reaction. The reactions may be summarised as follows :

$$NaOCl \rightleftharpoons Na^{\cdot} + OCl'$$
$$H_2O \rightleftharpoons H^{\cdot} + OH'$$
$$H^{\cdot} + OCl' \rightleftharpoons HOCl \text{ nearly undissociated ;}$$

which give, on addition :

$$NaOCl + H_2O \rightleftharpoons Na^{\cdot} + OH' + HOCl.$$

Now suppose that both the acid and base are weak. The ions of the salt now react with *both* the ions of water to form nearly undissociated acid and base. Thus, with ammonium hydrosulphide, we obtain ammonia and sulphuretted hydrogen (a weak acid) :

$$NH_4{\cdot}HS \rightleftharpoons NH_4^{\cdot} + HS'$$
$$H_2O \rightleftharpoons H^{\cdot} + OH'$$
$$H^{\cdot} + HS' \rightleftharpoons H_2S$$
$$NH_4^{\cdot} + OH' \rightleftharpoons NH_4{\cdot}OH$$

which give, on addition :

$$NH_4{\cdot}HS + H_2O \rightleftharpoons NH_4{\cdot}OH + H_2S \text{ ; or}$$
$$NH_4^{\cdot} + HS' + H_2O \rightleftharpoons NH_4{\cdot}OH + H_2S$$

since $NH_4{\cdot}HS$ is largely ionised in solution.

The reaction of the solution will now depend on the relative strengths of the acid and base. Since combination of both the anions of the acid, and the cations of the base, with $H^{\cdot}$ and OH' ions of water, respectively, occurs, the hydrolysis is greater in this case than when only the acid, or base, alone is weak.

Theory of indicators.—The action of acids and alkalies in changing the **colour** of certain substances has long been known, and utilised in testing for these two groups of compounds. Many natural colouring matters may be used for this purpose, the most important being **litmus**, a colour prepared from certain lichens (*Roccella tinctoria*, *Lecanora Tartarea*, etc.) growing on rocks near the sea.

Litmus comes into the market in small cubes, of a blue colour. These are powdered, and digested on a water-bath with water to which about one-fourth its volume of alcohol is added; the deep blue solution is decanted from the residue (calcium carbonate), filtered, and the free lime in the solution neutralised with dilute sulphuric acid until, after boiling, the solution has a purple colour. Filter paper soaked in the solution and dried forms **litmus paper.**

Turmeric papers (from an alcoholic extract of the ground root of the *Curcuma longa*, of India, used in making curries) are yellow, turned reddish-brown by alkalies or boric acid (p. 738). A number of synthetic organic substances are now also used as indicators.

Methyl-orange in aqueous solution is turned yellow by alkalies and red by acids; **paranitraniline** is colourless in acid solution, yellow in alkaline solution; **methyl-red** is turned red by traces of acids, and yellow by alkalies; **phenolphthalein** is colourless in acid solution, and is turned deep red by traces of alkali; **alizarin red** is turned deep purple by alkalies, yellow by acids.

According to **Ostwald's theory of indicators** (1894) these substances are **weak acids or bases,** one radical of which, in the ionic state, has a different colour from that in the undissociated molecule. Thus, **paranitraniline** is a weak acid, which in the undissociated state is colourless. A trace of strong acid added to its solution drives back the slight dissociation of the weakly acidic indicator in the aqueous solution, and the pale yellow solution becomes colourless. If, however, an alkali is added, the OH' ions combine with the $H^{\cdot}$ ions of the indicator to form H_2O molecules, and further ionisation of the weakly acidic indicator occurs. The anion of the indicator then exists in the solution in appreciable amounts, exhibiting a strong yellow colour.

In many of these reactions **changes of structure,** *i.e.*, of valency and the arrangement of the atoms, may occur in the radical when it leaves the neutral molecule to form an ion; this does not necessarily affect the above theory of indicators.

Phenolphthalein is supposed to function as a very weak acid; its salts, formed by the action of alkalies, are largely dissociated, giving an intensely red anion. Its action is similar to that of *p*-nitroaniline. **Methyl-orange** functions as a very weak base; its solutions contain traces of OH' ions and a red cation, whilst the undissociated substance is yellow, so that the aqueous solution of the indicator is orange-red. On addition of alkali, the ionisation of the indicator is forced back, and the yellow undissociated molecules are formed. The $H^{\cdot}$ ions of acids combine with the OH' ions of the indicator to form H_2O; further ionisation of the indicator takes place, and the red colour of the cation appears: $X{\cdot}OH \rightleftharpoons X^{\cdot}$ (red) $+ OH'$.

Sensitiveness of indicators.—An indicator requires a definite concentration of $H^{\cdot}$ or OH' ions to produce its characteristic colour change: this concentration varies with different indicators. Thus, **methyl-violet** is turned blue by a definite small concentration of strong acids (*e.g.*, H_2SO_4), whereas it is unchanged by the weak acetic acid at any concentration, since the latter can never produce the requisite concentration of $H^{\cdot}$ ions.

The ionic product $[H^{\cdot}] \times [OH']$ is constant in all aqueous solutions on account of the equilibrium: $H_2O \rightleftharpoons H^{\cdot} + OH'$, and equal to the dissociation constant of water: $[H^{\cdot}] \times [OH'] = 10^{-13{\cdot}8}$. The concentration of OH' ions required to produce a colour change of an indicator may, therefore, always be represented by the equivalent $H^{\cdot}$ ion concentration: $[OH'] = [OH'] \times [H^{\cdot}]/[H^{\cdot}] = 10^{-13{\cdot}8}/[H^{\cdot}]$. At the **neutral point** the $H^{\cdot}$ and OH' concentrations are equal, each being equal to its concentration in pure water: $[H^{\cdot}] = [OH'] = \sqrt{10^{-13{\cdot}8}} = 10^{-6{\cdot}9}$. If $[H^{\cdot}]$ is greater than $10^{-6{\cdot}9}$ the solution is *acid*; if it is less than $10^{-6{\cdot}9}$, *e.g.*, 10^{-8}, the solution is *alkaline*. The concentration of $H^{\cdot}$ ions may be represented by minus the exponent of the concentration, and is then usually written $p_{H^{\cdot}}$; *e.g.*, if $[H^{\cdot}] = 10^{-8{\cdot}1}$, $p_{H^{\cdot}} = 8{\cdot}1$. This is called the **sensitiveness** of the indicator. An **ideal indicator,** which shows the exact point of neutrality, corresponds with $p_{H^{\cdot}} = 6{\cdot}9$.

The values of the $H^{\cdot}$ ion concentrations required to produce colour changes of various indicators are given in the table below, compiled from the results of Salm (1906) and Sörensen (1909).

The gaps are to be filled in with the colour next adjoining, *e.g.*, phenolphthalein is colourless with all $H^{\cdot}$ concentrations greater than 10^{-8}, red for all less than this. It will be seen that litmus approaches an ideal indicator, *i.e.*, a solution reacting neutral to litmus is actually neutral: $[H^{\cdot}] = [OH'] = 10^{-6{\cdot}9}$; with phenolphthalein the solution would be still faintly alkaline; with methyl-orange it is slightly acid ($0{\cdot}0005N$); whilst methyl-violet requires $0{\cdot}01N$-acid to produce a colour change.

	N	Indicator.					
		Methyl-violet.	Methyl-orange.	Congo red.	Methyl-red.	Litmus.	Phenol-phthalein.
Colour of Indicator with Hydrogen-ion concentration normal multiplied by:—	2	Golden-yellow					
	1	Green					
	10^{-1}	Greenish-blue					
	10^{-2}	Blue	Red				
	10^{-3}	Violet	Orange-red	Blue	Violet-red		
	10^{-4}		Orange-yellow	Violet	Red		
	10^{-5}			Scarlet	Orange-yellow		
	10^{-6}				Yellow	Red	
	10^{-7}					Blue	Colourless
	10^{-8}						Rose-red
	10^{-9}						Red
	10^{-10}						
p.c. Indicator solution.		0·05	0·01	0·01	0·2 p.c. in 60 p.c. alcohol	—	0·05 in 50 p.c. alcohol
Drops indicator to 10 c.c. test.		3–8	5–10	3–5	4	—	3–20

EXPT. 149.—Three rows of five small flasks, each containing 100 c.c. of "conductivity" water (p. 212), are supported on a rack (Fig. 191) with milk-glass shelves. To the flasks of each row are added: *p*-nitrophenol, methyl-orange, litmus, phenolphthalein, and methyl-red, respectively. To the top row (*A*) a drop of baryta water is added, when the indicators give the *alkaline* reaction. To the bottom row (*C*) a drop of $N\ H_2SO_4$ is added; when the indicators give the *acid* reaction. To the middle row (*B*) 1 c.c. of very dilute baryta water is added from a burette, and then, by means of a series of small tubes fastened to a board, as shown, 1 c.c. of freshly distilled **methyl formate** is poured simultaneously into all the flasks of this row. The methyl formate slowly hydro-

lyses, giving methyl alcohol (neutral) and formic acid: $H{\cdot}COO{\cdot}CH_3 + H_2O = H{\cdot}COOH$ (formic acid) $+ CH_3{\cdot}OH$ (methyl alcohol). The $H^{\cdot}$ ions of the formic acid neutralise the OH' ions of the baryta, and then excess of $H^{\cdot}$ ions are formed. The solutions therefore change over from alkaline, through the point of exact neutrality, to acid. If the point of neutrality is taken as that corresponding with the colour change of litmus, the reactions of the other indicators, which change at different times, may be compared (Nernst, 1908).

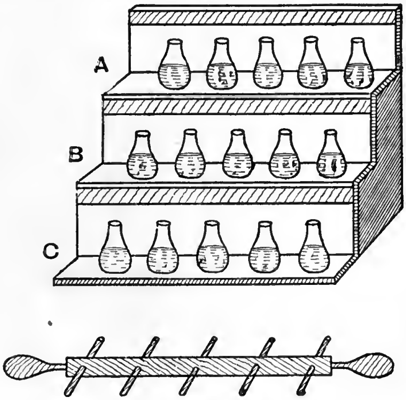


FIG. 191.—Experiment on Indicators.

SUMMARY OF CHAPTER XX

The **cause** of chemical change is identified with the **affinities** of the interacting substances, which may be electrical forces. The **activity** of a substance, which may be measured by the **velocity of reaction,** was shown by Berthollet (1799) to depend not only on its affinity, but also on its **concentration,** *i.e.*, the number of molecules in unit volume. The product of affinity and concentration is called the **active mass.**

The **Law of Mass-Action** states that the activity is proportional to the active mass, *i.e.*, to the concentration. *The product of the concentrations of the substances produced, divided by the product of the concentrations of the interacting substances, when equilibrium is attained, is constant:*

$$A + B + C + \dots \rightleftharpoons D + E + F \dots$$

$$\frac{[D] \times [E] \times [F] \dots}{[A] \times [B] \times [C] \dots} = K.$$

K is called the **equilibrium constant.**

EXERCISES ON CHAPTER XX

1. Point out the fallacy in the statement: "Potassium chlorate contains chlorine, although it gives no precipitate with silver nitrate."

2. Describe briefly the history of the theory of affinity until the time of Berthollet. What modifications did the latter introduce into the theory? It has been stated that: "the phrase 'active mass' commonly employed instead of the words 'molecular concentration' . . . is distinctly misleading." Criticise this assertion.

3. What experiments would you carry out in order to determine if the precipitation of bismuth chloride by water: $BiCl_3 + H_2O = BiOCl + 2HCl$, (*a*) is reversible; (*b*) is subject to the law of mass-action? The law of mass-action strictly applies only to homogeneous systems: defend its use in the present instance (*cf.* p. 358).

4. What would be the effect of increasing the pressure on the following systems in equilibrium: $N_2O_4 \rightleftharpoons 2NO_2$; $H_2O + CO \rightleftharpoons H_2 + CO_2$; $2SO_2 + O_2 \rightleftharpoons 2SO_3$; $N_2 + O_2 \rightleftharpoons 2NO$; $N_2 + 3H_2 \rightleftharpoons 2NH_3$? What the general law relating to such cases ?

5. If electric sparks are passed through a mixture of nitrogen and hydrogen, a little ammonia is formed : $N_2 + 3H_2 \rightleftharpoons 2NH_3$. How would you arrange an experiment in which a mixture of nitrogen and hydrogen is to be *completely* converted into ammonia ?

6. On what experimental evidence is it believed that acids, bases, and salts are ionised in aqueous solution ? Explain from this point of view (*a*) the alkaline reaction of sodium carbonate solution, (*b*) the acid reaction of copper nitrate solution.

7. It was considered that the atomic theory was fundamentally opposed to Berthollet's theory that *mass* produces an effect on chemical reactions (*cf.* p. 111). Explain how the two may be reconciled.

8. State briefly the modern theory of acids. Why are HCl and H_2SO_4 acids, whilst NH_3 and NaOH are not ? Discuss the place occupied by water, H_2O.

9. A solution of silver nitrate is added drop by drop to a solution of hydrochloric acid. In what way does the very slight solubility of silver chloride vary as the reaction proceeds up to and beyond the point when an equivalent amount of silver nitrate has been added ?

10. Discuss the theoretical foundation for the statement that endothermic compounds are more stable at high temperatures. Give examples. It is sometimes assumed that, at the temperature of the sun (6000°—10,000°) all compounds must be dissociated into their elements. Criticise this.

11. Explain how, when an acid solution is titrated with an alkaline solution, the neutral point may be determined from measurements of the electrical conductivity, without an indicator. Does the end-point obtained with an indicator necessarily indicate exact neutrality ? How is the latter defined ?

12. What explanation can you give of the fact that, although phenolphthalein is very sensitive to bases, it is insensitive to ammonia (a weak base) ? Why may methyl-orange be used ?

13. What is meant by *strong*, and *weak*, acids ? Arrange the following acids in the order of strength : acetic, nitric, sulphuric, carbonic, hydrochloric, hydrocyanic. What effects would aqueous solutions of the sodium salts of these acids have upon red and blue litmus papers ?

CHAPTER XXI

THE OXIDES AND OXY-ACIDS OF CHLORINE

The action of chlorine on alkalies. Hypochlorites.—If a stream of **chlorine** is passed through a **cold dilute solution of caustic potash,** a liquid smelling somewhat like chlorine, but with a distinct difference, is obtained. This liquid, discovered by Berthollet in 1789, possesses **bleaching properties,** and since it is more stable than chlorine water, it was used, under the name of **eau de Javelle,** for bleaching. This solution began to be used in England about 1798, but the absorption was carried out with milk of lime instead of with potash. Tennant, of St. Rollox (Glasgow), in 1799 found that chlorine is absorbed by dry slaked-lime, and the product, called **bleaching powder,** on treatment with water, gave a bleaching liquor.

The composition of these bleaching substances was investigated in 1842 by Balard, who showed that they contain salts of **hypochlorous acid,** HOCl. The reactions mentioned lead to the formation of a mixture of a **hypochlorite** and a chloride :

$$2KOH + Cl_2 = KCl + KOCl + H_2O.$$
$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O.$$

Instead of caustic potash, the cheaper caustic soda may be used, when a solution containing **sodium hypochlorite,** NaOCl, and sodium chloride, is formed. This solution is also produced by adding sodium carbonate solution to a solution of bleaching powder, and filtering off the precipitated calcium carbonate :

$$Ca(OCl)_2 + CaCl_2 + 2Na_2CO_3 = 2NaOCl + 2NaCl + 2CaCO_3,$$

or, more usually, by the electrolysis of brine under special conditions, so that the chlorine liberated at the anode is allowed to mix with the caustic soda produced at the cathode, and the liquid is kept cool.

The **bleaching action** of hypochlorites is due to **free hypochlorous acid,** HOCl, liberated by acids :

$$NaOCl + H_2SO_4 = NaHSO_4 + HOCl.$$

Even carbonic acid, *e.g.*, atmospheric carbon dioxide, turns out the very weak hypochlorous acid from its salts; hence solutions of these smell of the free acid when they have been exposed to air, and exhibit bleaching properties.

EXPT. 150.—Pass chlorine into cold dilute caustic soda solution. Take a piece of Turkey red cloth and paint on it a device with a mixture of gum and tartaric acid. Dry the cloth in a steam-oven and then immerse in the hypochlorite solution (containing a slight excess of alkali). The colour is discharged only where the acid was applied. Now pass a stream of carbon dioxide through the liquid: the colour is now completely discharged: $NaOCl + CO_2 + H_2O = NaHCO_3 + HOCl$.

The bleaching action of **hypochlorous acid** is due to **oxidation**: $HOCl = HCl + O$. Many colouring matters when oxidised yield colourless or feebly-coloured products.

Thus, **indigo blue,** $C_{16}H_{10}N_2O_2$, yields the yellow **isatin,** $C_8H_5NO_2$: $C_{16}H_{10}N_2O_2 + 2HOCl = 2C_8H_5NO_2 + 2HCl$. The yellow colour of unbleached cotton or linen is due to a natural brown colouring matter. In **bleaching** the yarn or fabric, it is first boiled with dilute caustic soda, to remove oily and resinous substances, and some colour. It is then washed, immersed in bleaching powder solution, and finally in dilute sulphuric acid, or exposed in piles to the air (carbonic acid). The acid sets free hypochlorous acid. The cellulose, of which the cotton fibres are composed, is resistant, unless the action is too prolonged, but the colour is oxidised. The remaining hypochlorous acid is removed by washing, and finally by treating with a substance such as sulphur dioxide, which decomposes the hypochlorous acid, and is hence called an **antichlor** (p. 522): $HOCl + SO_2 + H_2O = HCl + H_2SO_4$. Paper pulp, prepared from wood, is bleached with sodium hypochlorite solution and acid (p. 847).

Chlorine water.—The **bleaching action of chlorine water** may also be regarded as due to the hypochlorous acid it contains, although a considerable amount of free chlorine is present, since the reaction: $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$ is reversible.

The following equations:

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

show that hypochlorous acid, for the same weight of chlorine, has twice the bleaching activity of free chlorine. There is therefore no loss of bleaching activity when the chlorine is first absorbed by alkali, although half the chlorine is converted into inert chloride. It is the available *oxygen* liberated from HOCl which causes the bleaching action.

The **constitution of chlorine water,** explained above, may be proved by the following experiments. If chlorine water is distilled, hypochlorous acid comes over, leaving aqueous hydrochloric acid. In this case the equilibrium: $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$, is disturbed by the removal of the *volatile* constituent HOCl (or its anhydride, Cl_2O: $2HOCl \rightleftharpoons Cl_2O + H_2O$). The reaction therefore goes on practically to completion. But if chlorine water is boiled in a flask under a **reflux condenser** (Fig. 192), so that the distillate constantly flows back, it is not decomposed, but remains unchanged (Richardson, 1903). In this case the equilibrium is not disturbed, since no constituent is removed from the sphere of action.

Chlorates.—If excess of **chlorine** is passed through a **concentrated solution of caustic potash** or soda, the reaction is quite different from that which occurs with the cold dilute solution, described above.

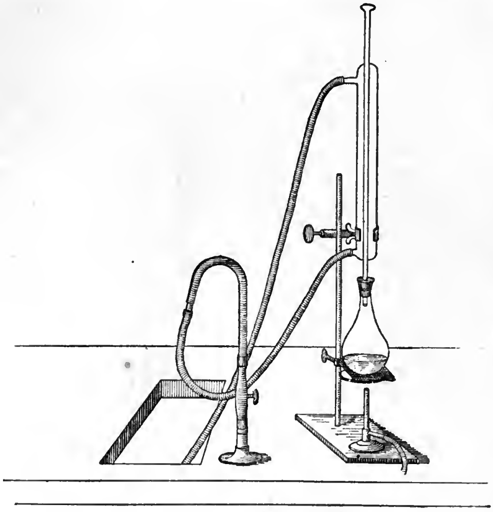


FIG. 192.—Reflux Condenser.

EXPT. 151.—The apparatus is shown in Fig. 193. Chlorine is generated from manganese dioxide and hydrochloric acid in the flask, washed with a little water, and passed into caustic potash solution (20 gm. of KOH in 40 c.c. of water) in the beaker. Crystals separate, and to prevent the delivery tube becoming choked, an inverted funnel is used. When the liquid smells strongly of chlorine, it is cooled, and decanted from the crystals which separate. If the decanted liquid is evaporated and allowed to cool, cubic crystals separate. These, on heating with concentrated sulphuric acid, give off fumes of hydrochloric acid: they consist of **potassium chloride.** The crystals obtained by decanting the original liquid are washed once or twice with a little cold water and then recrystallised from hot water. They have a tabular shape (Fig. 194), easily distinguishable from the cubes of chloride, and on heating in a test-tube melt and evolve oxygen, leaving potassium chloride. They consist of **potassium chlorate,** $KClO_3$.

The reaction is: $6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$.

Potassium chlorate, $KClO_3$, was discovered in this way by Berthollet in 1786; in accordance with Lavoisier's views on the nature of chlorine (p. 221) the new salt was called *hyperoxymuriate of potash.* Davy, however, showed that it was a triple compound of potassium, chlorine, and oxygen. Potassium chlorate gives certain **reactions** characteristic of all chlorates.

(1) Solutions of potassium chlorate give no precipitate with silver nitrate, but on heating the dry salt it gives off oxygen, and the residue when dissolved in water gives a white curdy precipitate of silver chloride with silver nitrate and dilute nitric acid: $2KClO_3 = 2KCl + 3O_2$; $KCl + AgNO_3 = AgCl + KNO_3$

(2) If a solution of potassium chlorate is mixed with indigo solution and sulphuric acid, and a few drops of sodium sulphite solution are added, the colour of the indigo is discharged. The chlorate is reduced by the sulphurous acid to a lower oxide of chlorine, which has strong bleaching properties.

(3) *A little* potassium chlorate treated with concentrated sulphuric acid in a test-tube turns orange-yellow, and evolves a yellow explosive gas (chlorine dioxide, ClO_2), having a peculiar odour (p. 380). On warming there is a crackling noise, due to explosions of the ClO_2.

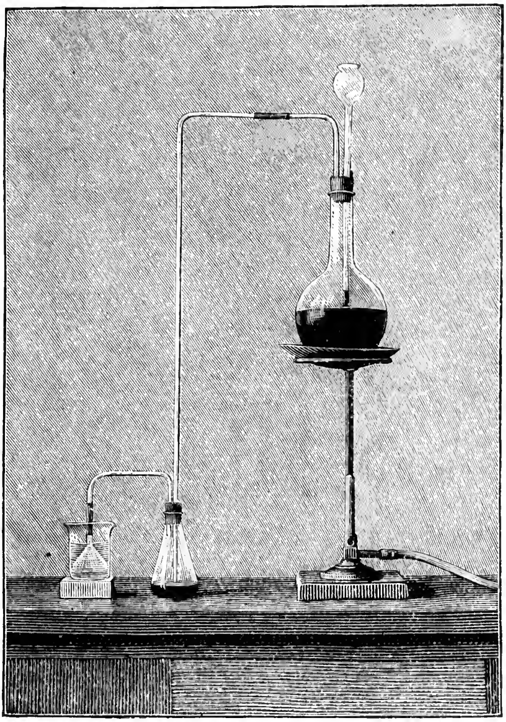


FIG. 193.—Preparation of Potassium Chlorate.

(4) Potassium chlorate warmed with concentrated hydrochloric acid gives off a yellow explosive gas (*euchlorine*), consisting of a mixture of Cl_2 and ClO_2: $8KClO_3 + 24HCl = 8KCl + 9Cl_2 + 12H_2O + 6ClO_2$.

Perchlorates.—In the decomposition of potassium chlorate by heat, another oxy-salt of chlorine is formed, viz., **potassium perchlorate**, $KClO_4$ (p. 161) : $4KClO_3 = 3KClO_4 + KCl$. This may also be prepared by fusing potassium chlorate with barium peroxide, extracting with hot water, and crystallising :

$$KClO_3 + BaO_2 = KClO_4 + BaO.$$

The salt was discovered by Stadion in 1816. It is hard to say what the oxymuriatic school would have called it ; the chlorate was already " hyperoxidised " according to their views. The crystalline form of the perchlorate differs from that of the chlorate (Figs. 5 and 195).

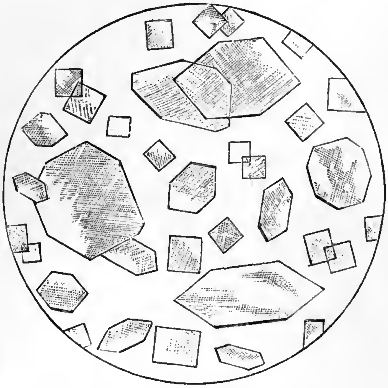


FIG. 194.—Crystals of Potassium Chlorate and Chloride.

Potassium perchlorate gives the following **reactions :**

(1) It decomposes at a higher temperature than the chlorate : $KClO_4 = KCl + 2O_2$.

(2) It does not bleach indigo in presence of sulphites.

(3) With concentrated sulphuric acid it does not give a yellow explosive gas, but dense white fumes of **perchloric acid**, $HClO_4$.

(4) It is not acted upon by hydrochloric acid.

Oxides and oxy-acids of chlorine.—By distilling hypochlorous acid under reduced pressure, it breaks up into water and its anhydride, **chlorine monoxide**: $2HOCl \rightleftharpoons Cl_2O\uparrow + H_2O$. Free **chloric acid** is formed, in aqueous solution, when potassium chlorate is decomposed by hydrofluosilicic acid, which gives a sparingly soluble potassium salt : $2KClO_3 + H_2SiF_6 = K_2SiF_6\downarrow + 2HClO_3$. By the action of chlorine dioxide on alkali, a chloride and a **chlorite** are formed : $2ClO_2 + 2KOH = KCl + KClO_2 + H_2O$. Perchloric acid when distilled under reduced pressure with phosphorus pentoxide gives its explosive anhydride, **chlorine heptoxide** : $2HClO_4 = H_2O + Cl_2O_7$.

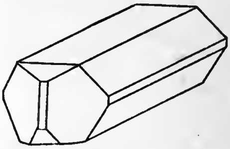


FIG. 195.—Crystal of Potassium Perchlorate.

The relations between the **oxygen compounds of chlorine** are given in the following table :

Oxides.			**Oxy-acids.**
Chlorine monoxide, or hypochlorous anhydride	Cl_2O	——→	**Hypochlorous acid,** HOCl
[Cl_2O_3 unknown] ...		- - - - - →	**Chlorous acid,** $HClO_2$
Chlorine dioxide, or chlorine tetroxide	ClO_2, or Cl_2O_4	↗ ↘	(chlorine dioxide is a **mixed anhydride,** *i.e.*, one giving salts of *two* acids with bases)
[Cl_2O_5 unknown] ...		- - - - -	**Chloric acid,** $HClO_3$
Chlorine heptoxide, or perchloric anhydride	Cl_2O_7	——→	**Perchloric acid,** $HClO_4$

Chlorine monoxide, Cl_2O.—This explosive substance is prepared by distilling concentrated hypochlorous acid under reduced pressure or by dehydrating it by the addition of fused calcium chloride: $2HOCl \rightleftharpoons Cl_2O + H_2O$. It is usually made by the action of dry chlorine on yellow precipitated oxide of mercury, previously heated to 300–400°, contained in a cooled tube (Fig. 196). A brown oxychloride of mercury remains, and chlorine monoxide gas passes on:

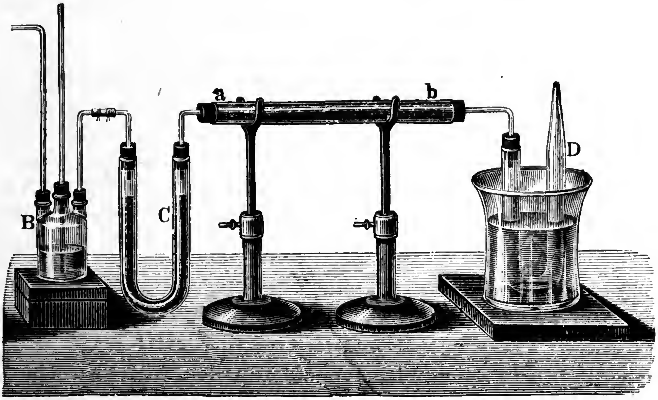


FIG. 196.—Preparation of Chlorine Monoxide.

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

It is condensed in a freezing mixture to an orange-coloured liquid, b.-pt. 5°. The brownish-yellow gas may be collected by downward displacement; it attacks mercury and is soluble in water.

The gas explodes readily, although not very violently, on heating, giving a mixture of two volumes of chlorine and one volume of oxygen: $2Cl_2O = 2Cl_2 + O_2$. In this way its composition may be determined. The chlorine after explosion is absorbed by caustic soda solution. The **liquid** may explode if the tube containing it is scratched with a file. If perfectly free from organic matter, however, it may be distilled without decomposition.

Hydrochloric acid is decomposed by the gas, with production of chlorine: $Cl_2O + 2HCl = 2Cl_2 + H_2O$. The gas dissolves easily in water, forming an orange-yellow solution containing **hypochlorous acid**: $Cl_2O + H_2O \rightleftharpoons 2HOCl$.

Hypochlorous acid, HOCl.—This acid is known only in solution. On distillation the latter breaks up into water and the anhydride of the acid, Cl_2O. A solution of the acid is obtained by shaking chlorine water with yellow precipitated mercuric oxide:

$$2Cl_2 + 2HgO + H_2O = HgCl_2{,}HgO + 2HOCl.$$

The liquid is distilled. The anhydride passing over recombines with water to form a dilute solution of hypochlorous acid, which collects in the receiver.

Hypochlorous acid is most conveniently prepared from **bleaching powder**, $Ca{\cdot}OCl{\cdot}Cl$.

When dissolved in water, bleaching powder is decomposed into chloride and hypochlorite: $2Ca{\cdot}OCl{\cdot}Cl = CaCl_2 + Ca(OCl)_2$. The same solution is formed by passing chlorine through cold milk of lime. If a clear solution of bleaching powder is treated with the calculated amount of 5 per cent. nitric acid, added slowly from a burette whilst the liquid is kept well stirred, hypochlorous acid is set free: $Ca(OCl)_2 + 2HNO_3 = Ca(NO_3)_2 + 2HOCl$. The liquid is then distilled, and a dilute solution of hypochlorous acid is obtained.

Any strong acid liberates from bleaching powder solution only hypochlorous acid as a primary product, if it is not added in excess:

$$Ca(OCl)_2 + H_2SO_4 = CaSO_4 + 2HOCl.$$

Hydrochloric acid reacts with hypochlorous acid with liberation of free chlorine: $HCl + HOCl \rightleftharpoons Cl_2 + H_2O$. If, therefore, an excess of any acid which is capable of liberating hydrochloric acid from calcium chloride is added to a solution of bleaching powder, the whole of the chlorine is expelled as such:

$$\underbrace{Ca(OCl)_2 + CaCl_2}_{2CaOCl_2} + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 2Cl_2.$$

Free hypochlorous acid is produced by the action of chlorine on a solution of a hypochlorite, *e.g.*, KOCl, or a solution of bleaching powder, which contains $Ca(OCl)_2$:

$$KOCl + Cl_2 + H_2O = KCl + 2HOCl.$$

This reaction probably occurs in two stages, as follows :

(a) $H_2O + Cl_2 \quad HCl + HOCl$.
(b) $KOCl + HCl = KCl + HOCl$.

The same result may be achieved by passing an excess of chlorine through milk of lime or baryta water, when a hypochlorite is first produced :

(a) $Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + H_2O$.
(b) $Ca(OCl)_2 + 2Cl_2 + 2H_2O = CaCl_2 + 4HOCl$.

If chlorine is passed through a suspension of sodium bicarbonate or precipitated calcium carbonate in water, hypochlorous acid (not a hypochlorite) is formed :

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

This reaction probably proceeds in two stages :

(i) $Cl_2 + H_2O \rightleftharpoons HCl + HClO$;
(ii) $HCl + CaCO_3 = CaCl_2 + CO_2 + H_2O$.

The hypochlorous acid produced is too weak to decompose the carbonate with formation of a hypochlorite. The function of the carbonate is to remove the hydrochloric acid as fast as it is produced, and so to prevent reaction (i) coming to a standstill.

Hypochlorous acid is also produced by passing chlorine through a solution of sodium sulphate or phosphate: $Na_2SO_4 + Cl_2 + H_2O = NaCl + NaHSO_4 + HClO$. In this case the hydrochloric acid formed as above reacts with the sodium sulphate: $Na_2SO_4 + HCl \rightleftharpoons NaHSO_4 + NaCl$. If the liquid is distilled, however, the hypochlorous acid may react with the sodium chloride to form sodium chlorate and free chlorine.

An interesting reaction is the formation of hypochlorous acid by the direct oxidation of hydrochloric acid, discovered by Odling in 1860 : $HCl + O = HOCl$. If a current of air is passed through concentrated hydrochloric acid in a wash-bottle, and then through potassium permanganate solution in a retort, warmed on a water-bath, hypochlorous acid distils over.

Hypochlorous acid in solution is pale yellow, or colourless when the solution is dilute. It is a very weak acid, practically un-ionised. The dilute solution is fairly stable in the dark : concentrated solutions decompose on heating, or exposure to sunlight, with evolution of oxygen and chlorine, and formation of some chloric acid :

(i) $2HOCl = 2HCl + O_2$;
(ii) $HCl + HOCl = H_2O + Cl_2$;
(iii) $HOCl + 2O \text{ (nascent)} = HClO_3$.

The decomposition is accelerated by platinum black, manganese dioxide, or the oxides of nickel and cobalt. Hypochlorites on heating with the latter oxides in alkaline solution rapidly evolve oxygen :

$2NaOCl = 2NaCl + O_2$. With concentrated acids they evolve chlorine, as described above.

The acid dissolves magnesium with evolution of hydrogen: $Mg + 2HOCl = Mg(OCl)_2 + H_2$. Iron and aluminium evolve hydrogen and chlorine; copper, nickel, and cobalt evolve chlorine and oxygen. With hydrogen peroxide the acid evolves oxygen:

$$HOCl + H_2O_2 = HCl + H_2O + O_2.$$

Hypochlorous acid is a powerful oxidising agent. Its bleaching action is due to the liberation of nascent oxygen: $HOCl = HCl + O$.

EXPT. 152.—Add caustic soda to a solution of manganous sulphate. A white precipitate of manganous hydroxide is formed: $MnSO_4 + 2NaOH = Mn(OH)_2 + Na_2SO_4$. Add sodium hypochlorite solution. The precipitate instantly becomes brown, and is converted into hydrated manganic oxide: $Mn(OH)_2 + NaOCl + H_2O = Mn(OH)_4 + NaCl$.

EXPT. 153.—To a solution of chrome alum add caustic soda; a green precipitate of chromic hydroxide, $Cr(OH)_3$, is formed. Add excess of NaOCl solution and NaOH, and boil. A yellow solution of sodium chromate, Na_2CrO_4, is formed: $2Cr(OH)_3 + 3NaOCl + 4NaOH = 2Na_2CrO_4 + 5H_2O + 3NaCl$.

Bleaching powder.—Chlorine gas does not react with quicklime at the ordinary temperature, but at a red heat oxygen is expelled and calcium chloride formed: $2CaO + 2Cl_2 = 2CaCl_2 + O_2$. If, however, chlorine is passed over dry *slaked* lime, $Ca(OH)_2$, it is rapidly absorbed, forming a somewhat moist powder which smells of hypochlorous acid, and is called **bleaching powder,** or **chloride of lime.** The reaction is: $Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O$, the water formed remaining principally in the powder.

In the **manufacture of bleaching powder** the slaked lime is spread over the floors of closed lead chambers, so as to expose a large surface, and somewhat diluted chlorine gas admitted. At first the chlorine is rapidly absorbed by the lime, but the reaction afterwards slows down. The powder is then turned over with wooden rakes, and the action of the gas continued until absorption is complete, which takes 12–14 hours. The product usually contains 37–39 per cent. of chlorine present as $CaOCl_2$, whereas that calculated from the formula $CaOCl_2 + H_2O$ is 49. Some free lime is also present.

With very dilute chlorine, such as is produced by the Deacon process, it is necessary to provide a very intimate contact of the lime with the gas. This is effected by making the gas traverse lead or iron pipes placed horizontally one above the other, through which the lime is pushed in the opposite direction to the gas by means of Archimedean screws (**Hasenclever screw-chambers,** Fig. 197). The lime drops from one pipe to the other and is withdrawn into casks at the bottom fully charged with chlorine.

The formula of bleaching powder.—Bleaching powder was at first regarded as a molecular compound of lime and chlorine—"chloride of lime," CaO,Cl_2. Balard in 1835 suggested that it was a *mixture* of equimolecular amounts of calcium hypochlorite and chloride: $Ca(OCl)_2 + CaCl_2$. Commercial bleaching powder always contains an excess of free lime, which led Stahlschmidt to assume that it contained the compound $Ca\begin{matrix}\diagup OH\\ \diagdown OCl\end{matrix}$, formed according to the equation:

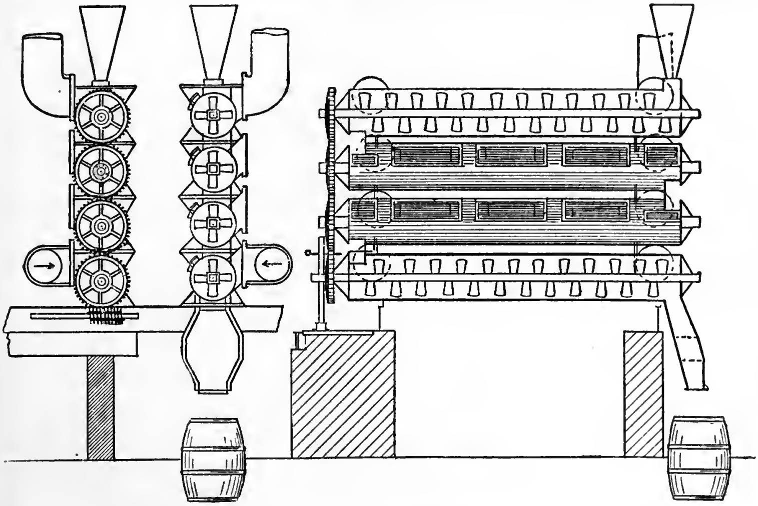
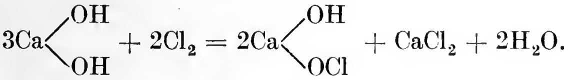


FIG. 197.—Hasenclever Bleaching Powder Apparatus.



$$3Ca\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} + 2Cl_2 = 2Ca\begin{matrix}\diagup OH\\ \diagdown OCl\end{matrix} + CaCl_2 + 2H_2O.$$

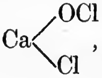
Later experiments showed, however, that free lime is not an essential constituent, but is merely due to the particles of lime becoming encrusted with bleaching powder, and so escaping complete chlorination. The reaction appears to be:

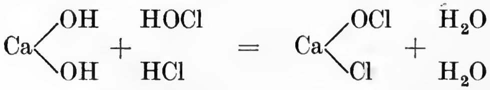
$$Ca(OH)_2 + Cl_2 = [CaOCl_2 + H_2O].$$

Lunge prepared a product of the following composition:

$CaOCl_2,H_2O$ =	91·80
$CaCO_3$	0·95
$CaCl_2$	0·45
$Ca(OH)_2$	6·80
	100·00

Balard's formula, $Ca(OCl)_2 + CaCl_2$, would require that bleaching powder should contain a considerable proportion of free calcium chloride. If, however, it is treated with successive small amounts of water, the first portions of the extract contain much less chlorine as chloride than would be the case if the latter pre-existed in the powder. Again, alcohol extracts from good bleaching powder only a small amount of calcium chloride, although the latter is readily soluble in that solvent.

These results agree with the formula proposed by Odling, according to which the active constituent of bleaching powder is a **mixed salt** of the formula  $\mathrm{Ca}\left\langle\begin{matrix}\mathrm{OCl}\\ \mathrm{Cl}\end{matrix}\right.$, *i.e.*, **calcium chloro-hypochlorite,** formed by the simultaneous neutralisation of a molecule each of hydrochloric and hypochlorous acids :



$$\mathrm{Ca}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. + \begin{matrix}\mathrm{HOCl}\\ \mathrm{HCl}\end{matrix} = \mathrm{Ca}\left\langle\begin{matrix}\mathrm{OCl}\\ \mathrm{Cl}\end{matrix}\right. + \begin{matrix}\mathrm{H_2O}\\ \mathrm{H_2O}\end{matrix}$$

Stahlschmidt's formula for the active constituent of bleaching powder, $Ca{\cdot}OH{\cdot}OCl$, is disproved by the fact that, although bleaching powder containing as much as 48·74 per cent. of chlorine which can be liberated by acids, *i.e.*, **available chlorine,** has been prepared, his formula limits this to 33 per cent.

O'Shea (1883) decided between the three rival formulæ :

Balard's $Ca(OCl)_2 + CaCl_2$,
Stahlschmidt's $Ca.OH.OCl$,
Odling's $Ca.OCl.Cl$,

as follows. He removed any free calcium chloride by treatment with alcohol, and determined in the residue : (i) the total lime, CaO ; (ii) the total chlorine ; (iii) the chlorine as hypochlorite. The following ratios were found :

lime : total chlorine = 1 : 2 ; lime : hypochlorite chlorine = 1 : 1;
hypochlorite chlorine : total chlorine = 1 : 2.

The residue after treatment with alcohol, and the above ratios, should be, in the different cases :

	Residue.	$\frac{CaO}{\text{total Cl}}$	$\frac{CaO}{\text{hypochlorite Cl}}$	$\frac{\text{hypochlorite Cl}}{\text{total Cl}}$
1. Balard ...	$Ca(OCl)_2$	1 : 2	1 : 2	1 : 1
2. Stahlschmidt ...	$Ca.OH.OCl$	1 : 1	1 : 1	1 : 1
3. Odling ...	$Ca.OCl.Cl$	1 : 2	1 : 1	1 : 2

Thus, only Odling's formula agrees with the experimental results.

Available chlorine of bleaching powder.—Bleaching powder is mainly employed as an **oxidising agent**, and the active agent is really the nascent oxygen of the hypochlorite. Usually, however, the chlorine equivalent of this active oxygen is returned as the **available chlorine** : O (16) = Cl_2 (71). If the bleaching powder consisted entirely of the compound Ca·OCl·Cl, the chlorine equivalent of the active oxygen atom of the hypochlorite radical would be O = Cl_2, *i.e.*, the *total* chlorine in the compound. This would, in fact, be wholly expelled by acids : $CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2$, in accordance with the former definition of available chlorine.

As it is met with in commerce, however, bleaching powder always contains some free calcium chloride, $CaCl_2$, and possibly calcium chlorate, $Ca(ClO_3)_2$, and since the chlorine of these compounds is not liberated as such by acids, and the oxygen of the chlorate is not available for the usual oxidising purposes of bleaching powder, a distinction is made between the total and available chlorine.

The **estimation of the available chlorine** of bleaching powder is carried out by one of the following methods :

1. **Penot's method** : About 10 gm. of bleaching powder are weighed out into a mortar, and triturated with successive quantities of cold distilled water until the paste has been transferred to a litre flask, which is filled to the mark with water, and well shaken. 50 c.c. of the well-shaken suspension (a little powder remains undissolved) are now pipetted into a beaker, and titrated with decinormal sodium arsenite solution, until a drop of the liquid, placed by means of a glass rod on a piece of filter-paper which has been soaked in potassium iodide and starch solution and dried, no longer gives a blue colour owing to liberation of iodine : $2KI + Cl_2 = 2KCl + I_2$. The reaction is : $As_2O_3 + 2CaOCl_2 = As_2O_5 + 2CaCl_2$. Thus As_2O_3 requires 2O or 4Cl ($4Cl + 2H_2O = 4HCl + 2O$), so that 1 c.c. of $\frac{N}{10}As_2O_3$ = 0·00352 gm. of active Cl.

The decinormal sodium arsenite, Na_3AsO_3, is prepared by dissolving 4·95 gm. of pure arsenious oxide, As_2O_3, and 25 gm. of pure sodium bicarbonate, $NaHCO_3$, in 500 c.c. of distilled water in a flask heated on a water-bath, cooling, and diluting to 1 litre in a measuring flask.

2. **Bunsen and Wagner's method** : 25 c.c. of the bleaching powder suspension are treated with excess of potassium iodide solution, and acidified with acetic acid. Iodine is liberated : $2KI + HOCl + CH_3{\cdot}COOH = 2CH_3{\cdot}COOK$ (potassium acetate) $+ I_2 + H_2O$. This is titrated with decinormal sodium thiosulphate solution until the yellow colour has practically vanished : $2Na_2S_2O_3 + I_2 = Na_2S_4O_6$ (sodium tetrathionate) + 2KI. A little starch-paste is then added, and the titration continued until the blue colour, due to the iodine, vanishes. $N/10$ $Na_2S_2O_3$ solution contains 24·8 gm. of $Na_2S_2O_3,5H_2O$ per litre ;

it is standardised by $N/10$-iodine solution. 1 c.c. = 0·00352 gm. of active Cl.

Hypochlorous acid, or hypochlorites, are estimated in presence of free chlorine by means of the following reactions:

$$2KI + HOCl + HCl = 2KCl + I_2 + H_2O$$
$$2KI + Cl_2 = 2KCl + I_2.$$

Each molecule of HOCl neutralises one equivalent of acid, whilst chlorine does not affect the acidity of the solution. By titrating the iodine and the remaining acid, the amounts of HOCl and Cl_2 may be calculated.

Hypochlorites.—A solution of **sodium hypochlorite** is prepared by methods previously described (p. 368). It is used in America for bleaching purposes instead of bleaching powder, and then contains 1 to 2 per cent. of NaOCl. By cooling a concentrated solution, from which sodium chloride has deposited, to $-10°$, and shaking, crystals of $NaOCl,6H_2O$, or $NaOCl,7H_2O$, separate. These are very deliquescent, and melt at 18°. On cooling the fused substance, large crystals of $NaOCl,5H_2O$ are formed.

Calcium hypochlorite, $Ca(OCl)_2$, is prepared in crystals by passing chlorine through milk of lime, and evaporating the clear solution *in vacuo*. It is more stable than bleaching powder, is completely soluble in water, and contains 80–90 per cent. available chlorine (theoretical hypochlorite oxygen in $Ca(OCl)_2 = 22{\cdot}4$ per cent., hence equivalent of $Cl = 22{\cdot}4 \times 70{\cdot}4/16 = 98{\cdot}5$ per cent.). The crystalline hydrate, $Ca(OCl)_2,4H_2O$, is first deposited on evaporation.

Chlorine dioxide, ClO_2 and Cl_2O_4.—By the action of concentrated sulphuric acid on potassium chlorate Davy (1815) obtained a yellow explosive gas. On explosion, two volumes of this gas gave three volumes of gas, consisting of two volumes of oxygen and one volume of chlorine, hence its formula is ClO_2:$2ClO_2 = Cl_2 + 2O_2$.

Powdered, previously fused, potassium chlorate is added in small quantities at a time to cooled concentrated sulphuric acid in a small retort. The orange-yellow paste is very cautiously warmed by placing the retort in lukewarm water, and the gas collected by downward displacement, since it is heavier than air. It dissolves in water and attacks mercury. There is considerable danger of violent explosion in the preparation of chlorine dioxide.

The reaction appears to take place as follows:

$$KClO_3 + H_2SO_4 = KHSO_4 + HClO_3 \text{ (chloric acid)};$$
$$3HClO_3 = HClO_4 \text{ (perchloric acid)} + 2ClO_2 + H_2O.$$

The **density** of chlorine dioxide gas was found by Pebal and Schacherl (1882) to correspond with the formula ClO_2. If passed through a tube cooled in a freezing mixture the gas condenses to a dark red **liquid**, boiling at 9°, and at − 79° this freezes to an orange-coloured crystalline **solid**. The liquid and solid are believed to have the formula Cl_2O_4. The liquid is violently explosive, although it may be distilled without decomposition in the entire absence of organic matter. The gas also explodes readily on heating with a hot wire or glass rod, by an electric spark, or in contact with turpentine, alcohol, or ether.

EXPT. 154.—Add a few c.c. of cold concentrated sulphuric acid to two portions of 1 gm. of potassium chlorate in two test-tubes. A yellow gas with a peculiar smell is generated. Insert a hot glass rod into one tube ; into the other throw a small piece of phosphorus. The gas in the first tube explodes ; the phosphorus in the second tube inflames spontaneously and explodes the gas.

Chlorine dioxide (sometimes called **chlorine peroxide**) is a **powerful oxidising agent.** This is evident from some of the following experiments.

EXPT. 155.—Equal parts of powdered sugar (or starch) and potassium chlorate are mixed with a spatula on a piece of paper, and a drop of concentrated sulphuric acid is allowed to fall on the mixture from a glass rod. The whole mass ignites, and burns violently.

EXPT. 156.—A little potassium chlorate is placed in a glass of water, and one or two small fragments of phosphorus are thrown in. If a few c.c. of concentrated sulphuric acid are poured carefully down a thistles funnel on to the chlorate, ClO_2 is evolved. When the bubbles of this gas come in contact with the phosphorus, there is a series of flashes of light, accompanied by slight and harmless explosions.

EXPT. 157.—Chlorine dioxide, generated from 1 gm. of previously fused chlorate and 3 c.c. of cold concentrated sulphuric acid in a small jar, is decanted into a second jar containing leaves of Dutch metal. No action occurs. The gas is then exploded by a hot wire, when the metal at once takes fire in the chlorine liberated.

EXPT. 158.—A drop of a solution of phosphorus in carbon disulphide is allowed to fall on a *small* quantity of powdered potassium chloride. When the carbon disulphide has evaporated there is a sharp explosion.

Chlorous acid, $HClO_2$.—Chlorine dioxide dissolves in water, forming a yellow solution without acid reaction. With solutions of alkalies, however, it acts as an acidic oxide, forming a mixture of two salts in equivalent amounts : $2KOH + 2ClO_2 = KClO_3 + KClO_2 + H_2O$. It is a mixed anhydride, forming the salts of two acids with bases. $KClO_2$ is the salt of **chlorous acid,** $HClO_2$. The two salts may be separated by evaporation *in vacuo* over sulphuric acid, when the less soluble $KClO_3$ is first deposited.

Pure chlorites may be obtained by the action of alkali and hydrogen peroxide on a concentrated aqueous solution of chlorine dioxide. The latter is conveniently prepared by warming to 60° a mixture of 40 gm. of $KClO_3$, 150 gm. of crystalline oxalic acid, and 20 c.c. of water, and passing the gas into water: $2KClO_3 + 2C_2H_2O_4 = K_2C_2O_4 + 2H_2O + 2CO_2 + 2ClO_2$. When diluted with carbon dioxide, chlorine dioxide is not liable to explode during preparation. The hydrogen peroxide reduces chlorine dioxide to chlorous acid: $2ClO_2 + H_2O_2 = 2HClO_2 + O_2$.

The alkali chlorites have a caustic taste, and bleach vegetable colours. They may be distinguished from hypochlorites by the bleaching action *after* addition of sodium arsenite. Silver and lead nitrates precipitate yellow crystalline $AgClO_2$ and $Pb(ClO_2)_2$. These explode on heating; lead chlorite detonates violently on percussion when mixed with sugar, and is used for detonators. Free chlorous acid is obtained in solution by treating a chlorite with oxalic acid.

The anhydride of chlorous acid would be Cl_2O_3, but is not known. The gas prepared by heating a mixture of potassium chlorate and sugar, benzene, or arsenious oxide, with nitric acid, believed to be the trioxide of chlorine by Millon (1845), was shown by Garzarolli-Thurnlack and Schacherl to be a mixture of chlorine dioxide with chlorine. The mixture of chlorine and the dioxide obtained by treating potassium chlorate with concentrated hydrochloric acid, supposed by Davy to be an oxide of chlorine, and called **euchlorine,** was examined by Pebal, and the method used was applied by the above experimenters to the supposed trioxide.

A measured volume of the gas was exploded by heating, and the increase in volume determined. The chlorine was then absorbed by potash solution, and the residual oxygen measured. A comparison of the expansion on explosion with the volume of oxygen produced showed that the latter was double the former.

The different oxides of chlorine would give the following results:

	Expansion on Explosion.	Residual oxygen after absorption of chlorine.
(1) Chlorine monoxide : Cl_2O		
$2Cl_2O = 2Cl_2 + O_2$	$3 - 2 = 1$ vol.	1 vol.
(2) Chlorine dioxide, ClO_2		
$2ClO_2 = Cl_2 + 2O_2$	$3 - 2 = 1$ vol.	2 vols.
(3) Chlorous anhydride, Cl_2O_3 (?)		
$2Cl_2O_3 = 2Cl_2 + 3O_2$ ...	$5 - 2 = 3$ vols.	3 vols.

With euchlorine and the supposed trioxide, the volume relations (2) were found, hence both contained only chlorine and chlorine dioxide. By passing the "trioxide," and euchlorine, through tubes immersed in a freezing mixture, pure chlorine dioxide was liquefied, and chlorine passed on.

Chloric acid, $HClO_3$.—**Chloric acid** is much more stable than hypochlorous acid; it is formed when the latter, or chlorine water, is exposed to light. If a solution of potassium chlorate is precipitated with hydrofluosilicic acid, sparingly soluble potassium silicofluoride is formed, and the aqueous chloric acid can be filtered off: $2KClO_3 + H_2SiF_6 = K_2SiF_6 + 2HClO_3$. It is most convenient to start with **barium chlorate,** a solution of which is precipitated with the calculated amount of sulphuric acid: $Ba(ClO_3)_2 + H_2SO_4 = BaSO_4$ (ppd.) $+ 2HClO_3$. The solution is decanted from the barium sulphate, and evaporated in a vacuum desiccator over concentrated sulphuric acid until it contains 40 per cent of $HClO_3$. On further concentration the acid decomposes into chlorine, oxygen, and perchloric acid.

Barium chlorate is made by evaporating a solution of sodium chlorate and barium chloride: $2NaClO_3 + BaCl_2 \rightleftarrows 2NaCl + Ba(ClO_3)_2$. The sodium chloride is deposited, and is fished out: the remaining solution is crystallised. Chloric acid was prepared from barium chlorate by Gay-Lussac in 1814. The concentrated acid is colourless, and fairly stable in the dark. When exposed to light it undergoes decomposition (see above) and becomes yellow. Organic substances, such as cotton-wool or paper, are ignited by the concentrated acid. It has a pungent smell, and strong acidic and bleaching properties. The anhydride corresponding with chloric acid, $2HClO_3 - H_2O = Cl_2O_5$, is not known.

EXPT. 159.—Pour a concentrated solution of sodium hydrogen sulphite ($NaHSO_3$) over crystals of potassium chlorate. A trace of free chloric acid is liberated by the weakly acid $NaHSO_3$. The latter is then oxidised by the chloric acid to the strongly acid $NaHSO_4$. More chloric acid is liberated, and the velocity of reaction is increased by the action of the products (*i.e.*, by **autocatalysis**) until in one or two minutes the whole mixture foams over, acid sodium sulphate ($NaHSO_4$) and hydrochloric acid being formed.

Chloric acid is ionised in solution, and is a strong acid: $HClO_3 \rightleftarrows H^{\cdot} + ClO'_3$. In acid solutions chlorates are readily reduced by iron or aluminium powder to hydrochloric acid. In this way they may be estimated: $HClO_3 + 3H_2 = 3H_2O + HCl$.

Perchloric acid, $HClO_4$.—The most stable oxy-acid of chlorine is that containing most oxygen, viz., **perchloric acid,** $HClO_4$. Small quantities of the very soluble sodium salt, $NaClO_4$, occur in Chile nitre (p. 563): they act prejudicially on vegetation if the impure nitrate is used as a fertiliser.

Perchloric acid is formed by the evaporation of a solution of chloric acid, and if the latter is distilled, aqueous perchloric acid comes over, chlorine and oxygen escaping at the same time.

Potassium perchlorate, $KClO_4$, is prepared by heating the chlorate at about 400° until it becomes pasty, and separating from the more soluble chloride by crystallising from hot water: $2KClO_3 = KClO_4 + KCl + O_2$, or $4KClO_3 = 3KClO_4 + KCl$. Any chlorate remaining may be decomposed by hydrochloric acid, which is without action on the perchlorate. If potassium perchlorate is distilled with four times its weight of very concentrated sulphuric acid in a small retort, perchloric acid comes over as a colourless, or slightly yellow, strongly fuming liquid: $KClO_4 + H_2SO_4 = KHSO_4 + HClO_4$. The yield is increased by carrying out the distillation under 10–20 mm. pressure, when the acid distils over between 90° and 160°. It is purified by distilling under 60 mm. pressure, when it boils at 40–60°. It boils, with partial decomposition, at 90° under 760 mm. pressure, or without decomposition at 19° under 11 mm. pressure.

During the distillation under ordinary pressure, the liquid in the receiver gradually solidifies to white crystals of the monohydrate, $HClO_4,H_2O$, m.-pt. 50°. Other crystalline hydrates are known: $HClO_4,2H_2O$ (m.-pt. $-20{\cdot}6°$); $2HClO_4,5H_2O$ (m.-pt. $-30°$); and two forms of $HClO_4,3H_2O$ (m.-pt. $-43{\cdot}2°$ and $-37°$). The anhydrous acid is very hygroscopic, and dissolves in water with a hissing noise and great evolution of heat. The hydrate $HClO_4,H_2O$ was regarded as the acid itself by its discoverer, Stadion (1816); pure $HClO_4$ was first prepared by Roscoe (1863). On heating, $HClO_4,H_2O$ breaks up into anhydrous acid, which distils over, and an oily solution of maximum boiling point, 203°, containing 72 per cent. of $HClO_4$.

The oily aqueous acid, which is quite stable, is conveniently prepared by adding ammonium perchlorate (a commercial substance), dissolved in concentrated hydrochloric acid, to warm concentrated nitric acid in a porcelain dish. Nitrogen, chlorine, and nitrosyl chloride are evolved, and on evaporation aqueous perchloric acid remains:

$$\begin{aligned} &NH_4ClO_4 + HCl = NH_4Cl + HClO_4 \\ &HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O \\ &2NH_4Cl + 3Cl_2 = N_2 + 8HCl. \end{aligned}$$

Anhydrous perchloric acid is liable to explode spontaneously; paper and wood catch fire when it is dropped on them. If a few drops of the acid are poured on recently-ignited wood charcoal, there is a violent explosion.

The aqueous acid dissolves iron and zinc to form perchlorates: $2HClO_4 + Zn = Zn(ClO_4)_2 + H_2$, and the acid is not reduced (*cf.* $HClO_3$). It is reduced only by sodium hyposulphite ($Na_2S_2O_4$), titanium trichloride, or, in alkaline solution, by ferrous hydroxide. It is therefore a much less powerful oxidising agent than chloric acid.

The preparation of acids.—The preparations of perchloric and chloric acids illustrate two **general methods for the preparation of acids.** A **salt** of the acid is acted upon by another acid. A state of equilibrium then results, in which all four compounds are present $RX + HA \rightleftharpoons RA + HX$. It may not be possible in practice to separate the acid HX from the other substances, but if it can be separated, the equilibrium is disturbed, and the reaction may go on nearly to completion. Separation is possible when **the acid HX is volatile,** as in the case of perchloric acid. It is then distilled off. If the acid is not appreciably volatile, as in the case of chloric acid, a second method may be used. In this, the salt RX and the acid HA are so chosen that **the salt RA is practically insoluble**; it is then filtered off, and the acid HX is left in solution.

Thus R may be $Ba^{\cdot\cdot}$ or $K^{\cdot}$, and A, SO_4'' or SiF_6'' respectively, since $BaSO_4$ and K_2SiF_6 are only sparingly soluble in water. It will be found that nearly all the methods described for the preparation of acids from their salts are special cases of these two general methods.

Chlorine heptoxide, Cl_2O_7.—The anhydride of perchloric acid, Cl_2O_7, was discovered by Michael and Conn in 1900. 10 gm. of phosphorus pentoxide are placed in a small stoppered retort connected with a phosphorus pentoxide drying-tube and a receiver cooled in ice and salt. Pure perchloric acid is added, in quantities of 10 drops at a time, and allowed to trickle down the sides of the retort on to the P_2O_5: an interval of ten minutes is allowed to elapse after each addition, and the retort is kept at a temperature of $-10°$ in a freezing mixture. After allowing to stand twenty-four hours in the freezing mixture, the retort is warmed to 85°, and a colourless oily liquid distils over, boiling at 82°. This is **perchloric anhydride,** Cl_2O_7: $2HClO_4 - H_2O = Cl_2O_7$. Violent explosions may occur in its preparation, although Cl_2O_7 is more stable than Cl_2O or ClO_2, and may be poured on paper, wood, sulphur, or phosphorus, without explosion. It explodes when heated or struck, and decomposes on standing for a few days. It sinks in water, and slowly forms $HClO_4$: $Cl_2O_7 + H_2O = 2HClO_4$.

The manufacture of chlorates and perchlorates.—**Chlorates** are manufactured either by the action of excess of chlorine on concentrated solutions of alkalies, or by the electrolysis of chlorides. **Calcium chlorate** is produced by passing chlorine into hot milk of lime contained in cast-iron vats, with agitating paddles (Fig. 198), until the reaction is complete. Lunge and Landolt represent the reaction as follows:

(1) $2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + H_2O$.
(2) $Ca(OCl)_2 + 2Cl_2 + 2H_2O = CaCl_2 + 4HClO$.
(3) $2Ca(OCl)_2 + 4HClO = CaCl_2 + Ca(ClO_3)_2 + 2Cl_2 + 2H_2O$.

The complete reaction is: $6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$, but this appears to take place with the intermediate formation of hypochlorous acid, which acts as a carrier of oxygen. The action of heat alone on calcium hypochlorite, in the absence of excess of chlorine, is mainly according to the equation: $Ca(OCl)_2 = CaCl_2 + O_2$. Alkaline hypochlorite solutions may be boiled without much decomposition, but oxygen is slowly evolved. Traces of chlorites are also formed.

The solution of calcium chlorate may be treated with potassium chloride, when the sparingly soluble **potassium chlorate** crystallises out, and is recrystallised. It is now usual to produce the very soluble **sodium chlorate,** $NaClO_3$. The solution of calcium salts is concentrated, cooled, and filtered from the crystals of hydrated calcium chloride which separate. Excess of sodium sulphate is then added, when all the calcium is precipitated as sulphate. On evaporation of the filtered solution, sodium chloride separates; this is removed, and, on cooling, sodium chlorate crystallises out.

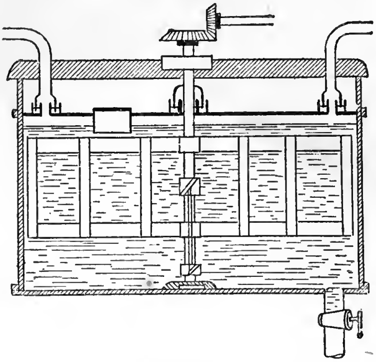


FIG. 198.—Manufacture of Calcium Chlorate.

Chlorates and perchlorates are also produced by the **electrolysis** of saturated sodium chloride solution at 80°, between platinum electrodes placed close together. A little potassium chromate is added as a catalyst. The chloride is first completely converted into **chlorate**; on prolonged electrolysis, this passes into **perchlorate.** There are large chlorate works in Switzerland and at Niagara. Chlorates are used as oxidising agents (*e.g.*, in the oxidation of aniline to aniline black), and in making fireworks. Perchlorates are employed in the manufacture of detonators and explosives.

Heat of reaction.—The evolution of heat which accompanies large numbers of chemical reactions, in some cases appearing as active combustion, is of great importance in technical processes. The greater part of the energy expended in the affairs of daily life proceeds from the combustion of coal, in other words from a chemical process. The value of coal is not in its chemical constituents, since these are almost entirely dissipated and lost in the ashes and flue-gases during its combustion, but is determined by the amount of **energy** in the form of heat which can be obtained by the combustion of the fuel.

It follows from the Law of Conservation of Energy that the energy contained in the unburnt coal, and in the oxygen of the air, must exceed that in the ash, and in the gaseous products of combustion, by the amount of heat evolved. The latter is thus a measure of the difference between these two stores of energy.

The stores, or charges, of **chemical energy** associated with material systems may be set free in the form of heat (or electrical energy, p. 879) during chemical reactions. In these changes, however, only a portion of the energy of the materials is set free; another part remains associated with the products. How much energy is associated with matter we have no certain means of judging; all that can be determined is the difference between the energies of the systems before and after change has occurred. This difference is evolved as **heat,** and may be measured.

If the reacting matter is in the gaseous form, considerable changes of volume may occur, and hence **work** is done by the pressure of the atmosphere on the system, if there is a contraction, or is spent by the system in overcoming that pressure, if there is an expansion. In the former case, the evolution of heat is greater, by the thermal equivalent of the external work, than it would have been if no change of volume had occurred. In the latter case, the heat evolved is diminished by that part of the energy of the system which would otherwise have appeared as heat, but now leaves the system as external work spent in overcoming pressure. To obtain the net diminution of energy of the system, the reaction must be carried out at constant volume; or, if the volume changes, a correction for the external work must be applied to the heat evolved. If there is contraction, work is spent on the system and appears as heat, so that this must be subtracted from the total heat evolved. If there is expansion, part of the energy appears as work, and its equivalent in heat must be added to the observed heat evolution.

We have therefore to distinguish between **heats of reaction at constant volume** and **heats of reaction at constant pressure.**

A mixture of 2 gm. of H_2 and 16 gm. of O_2 at 0° and 1 atm. pressure occupies $22{,}240 + 11{,}120 = 33{,}360$ c.c. If this is converted into liquid water at 0°, the latter will occupy 18 c.c. There has been a diminution in volume of $33{,}360 - 18 = 33{,}342$ c.c., and since the atmospheric pressure is equal to $76 \times 13{\cdot}6 \times 981$ dynes per sq. cm. (p. 149), the work done by the atmospheric pressure on the system, which appears as heat, is $33{,}342 \times 76 \times 13{\cdot}6 \times 981 = 3{\cdot}38 \times 10^{10}$ ergs $= 3{\cdot}38 \times 10^{10}/4{\cdot}18 \times 10^7$ gm. cal. $= 808{\cdot}5$ gm. cal. The observed **heat of reaction at constant pressure** is 68,939 gm. cal., hence the **heat of reaction at constant volume** is $68{,}939 - 808{\cdot}5 = 68{,}130$ gm. cal. This latter value represents the difference between the chemical energies of the hydrogen and oxygen gases, and that of the liquid water. Thus:

$$2H + O = H_2O \text{ (liq.)} + 68{,}939 \text{ gm. cal. (constant pressure)}$$
$$2H + O = H_2O \text{ (liq.)} + 68{,}130 \text{ gm. cal. (constant volume).}$$

If the reaction occurred at 100°, with production of steam, the heat evolved is diminished by the latent heat of steam, 18 × 538 gm. cal.

Hess's law.—If a reaction is carried out in stages, the algebraic sum of the amounts of heat evolved in the separate stages (heat absorbed being reckoned negative) **is equal to the total evolution of heat when the reaction occurs directly.**

This simple consequence of the **Law of Conservation of Energy** is known as **Hess's Law** (1840). It enables one to calculate many heats of reaction which could not be determined directly.

EXAMPLE 1.—Find the heat of formation of carbon monoxide, CO, from solid carbon and gaseous oxygen, given the following data:

Heat of combustion of carbon to carbon dioxide: $C + 2O = CO_2 + 97$ kgm. cal.

Heat of combustion of carbon monoxide to dioxide: $CO + O = CO_2 + 68$ kgm. cal.

By subtracting the second of these equations from the first, we find:

Heat of formation of carbon monoxide: $C + O = CO +$ **29 kgm. cal.**

EXAMPLE 2.—Find the heat of formation of ammonia from its elements, given:

(1) $2NH_3 + 3O = 3H_2O$ (liq.) $+ N_2 + 18{,}120$ gm. cal.

(2) $2H + O = H_2O$ (liq.) $+ 68{,}939$ gm. cal.

Multiply (2) by 3, and subtract from (1):

$$2NH_3 + 3O - 6H - 3O = 3H_2O + N_2 - 3H_2O + 18{,}120 - 206{,}871.$$

$$\therefore\ N_2 + 3H_2 = 2NH_3 + 188{,}697 \text{ gm. cal.};$$

$$\therefore\ N + 3H = NH_3 + \mathbf{94{,}348} \textbf{ gm. cal.}$$

Heats of formation are calculated for 1 gm. mol. of the compound.

Thermochemistry.—That branch of chemistry which is concerned with heats of reaction is called **thermochemistry**. The fundamental law is that of Hess, and by means of this all heats of reaction may be calculated from the heats of formation of the compounds concerned. These **heats of formation** have been determined experimentally, chiefly by Julius Thomsen, and by Marcellin Berthelot, and are tabulated per **gm. mol.** of compound produced.

If we suppose all the compounds on the left of an equation to be decomposed into their elements, an amount of heat is absorbed equal to the algebraic sum of the heats of formation of these compounds. If we now suppose the elements to be combined to form the compounds on the right of the equation, an amount of heat is evolved equal to the algebraic sum of the heats of formation of these compounds. It follows from Hess's law that:

Heat of reaction = Heat of formation of final compounds — Heat of formation of initial compounds.

The energies of the compounds are all referred to those of the elements as zero. The amounts of energy associated with the different elements are not, of course, zero, nor are they equal, but it is only the difference between the amounts of energy associated with the elements when in combination and when free that is required.

Thus, the equation $Cu + Cl_2 = CuCl_2 + 51{\cdot}6$ kg. cal. may be written in the form: $0 = CuCl_2 + 51{\cdot}6$ kg. cal., or $CuCl_2 = -51{\cdot}6$ kg. cal., indicating that $CuCl_2$ contains 51·6 kg. cal. less energy than $Cu + Cl_2$. *The symbols of compounds thus represent quantities of energy, which may be added or subtracted.* We may therefore, in the thermochemical equation, write the negative values of the heats of formation instead of the chemical symbols, and solve for the unknown heat of reaction.

EXAMPLE 3.—Find the heat of the reaction:

$$CaCl_2 + 2Na = Ca + 2NaCl + x.$$

The heats of formation of $CaCl_2$ and NaCl are 170 kg. cal. and 97·8 kg. cal., respectively, hence:

$$-170 = -2 \times 97{\cdot}8 + x, \quad \text{or} \quad x = \mathbf{25{\cdot}6\ kg.\ cal.}$$

If substances are produced in aqueous solution, we have to take account of the **heats of solution.** These vary with the amount of water, but become constant when this is very large; we usually suppose so much water taken that the heat of solution is constant. This amount of water is denoted by Aq. Thus: NH_3 (gas) + Aq = NH_3,Aq + 8400 gm. cal. means that when 17 grams of ammonia gas dissolve in a large quantity of water, 8400 gm. cal. are evolved. If still more water is added, no heat change occurs, hence Aq does not need to be specially stated. The heat of solution of perchloric acid is very large: $HClO_4$ + Aq = $HClO_4$,Aq + 20,100 gm. cal.

The stability of compounds.—We have frequently used the terms **stable** and **unstable** to denote whether a given compound is with difficulty resolved into its elements, or into related compounds, or whether this change takes place easily and spontaneously. Thus, water and hydrogen chloride are stable compounds: they show no tendency to decompose spontaneously into their elements, or into other compounds of these. The oxides and oxy-acids of chlorine, on the other hand, are all unstable substances, decomposing spontaneously, or when heated, or when brought in contact with other substances. We have also seen that there are different **degrees of stability**; thus the stability of perchloric acid is greater than that of hypochlorous acid.

It is of interest to inquire into the **causes of the stability** (or otherwise) of **substances.** Formerly only certain empirical rules, which had numerous exceptions, were available for this inquiry.

Thus, the stability of a compound depends on the **electrochemical**

character (and therefore on the position in the Periodic System, *cf.* p. 455) of its component elements. Compounds of strongly electropositive with strongly electronegative elements are usually stable, *e.g.*, $\overset{+}{\mathrm{K}}\overset{-}{\mathrm{Cl}}$; whilst compounds of elements of the same electrochemical character are usually unstable, *e.g.*, $\overset{-}{\mathrm{Cl}}_2\overset{-}{\mathrm{O}}$, $\overset{+}{\mathrm{Pd}}_2\overset{+}{\mathrm{H}}$. An exception is the very stable $\overset{-}{\mathrm{P}}_2\overset{-}{\mathrm{O}}_5$. Again, the stability of a compound alters with the **valency** of an element contained in it. Thus $\overset{\mathrm{IV}}{\mathrm{Pt}}\mathrm{Cl}_4$ decomposes at 300° into $\overset{\mathrm{II}}{\mathrm{Pt}}\mathrm{Cl}_2$ and Cl_2 ; $\overset{\mathrm{II}}{\mathrm{Pt}}\mathrm{Cl}_2$ is decomposed only at 500°, and is therefore more stable. The **atomic linkage** also affects the stability ; in carbon compounds, those which are saturated (single linkages) are much more stable than those which are unsaturated, or contain double or treble bonds (p. 250). Thus, ethane, $\mathrm{CH_3{\cdot}CH_3}$, is quite stable, whereas acetylene, $\mathrm{CH}\vdots\mathrm{CH}$, is explosive.

The principal condition affecting the stability of a substance, however, is the **quantity of energy** it contains.

If we examine the thermochemical equations :

$$\begin{aligned}
&2\mathrm{H} + \mathrm{O} = \mathrm{H_2O}\ (\text{liq.}) + 68{\cdot}4\ \text{kg. cal.}\\
&\mathrm{H} + \mathrm{Cl} = \mathrm{HCl} + 22\ \text{kg. cal.}\\
&\mathrm{K} + \mathrm{Cl} = \mathrm{KCl} + 106\ \text{kg. cal.}\\
&\mathrm{C} + 2\mathrm{H_2} = \mathrm{CH_4} + 21{\cdot}8\ \text{kg. cal.}
\end{aligned}$$

we see that all the above compounds, water, hydrochloric acid, potassium chloride, and methane, are formed from their elements with considerable **evolution of heat,** *i.e.*, **loss of energy**—*i.e.*, they are strongly **exothermic compounds.** They contain considerably less energy than the elements from which they are produced, and their properties show that they are **stable.**

Now consider the following thermochemical equations :

$$\begin{aligned}
&2\mathrm{Cl} + \mathrm{O} = \mathrm{Cl_2O} - 17{\cdot}8\ \text{kg. cal.}\\
&\mathrm{HCl,Aq} + \mathrm{O} = \mathrm{HOCl,Aq} - 9{\cdot}3\ \text{kg. cal.}\\
&\mathrm{HCl,Aq} + 3\mathrm{O} = \mathrm{HClO_3,Aq} - 15\ \text{kg. cal.}\\
&\mathrm{HCl,Aq} + 4\mathrm{O} = \mathrm{HClO_4,Aq} - 0{\cdot}7\ \text{kg. cal.}
\end{aligned}$$

The compounds chlorine monoxide, hypochlorous acid, chloric acid, and perchloric acid are formed from the substances on the left with **absorption of heat** ; they are **endothermic compounds,** and contain *more* energy than their constituents. They are all unstable, and tend to decompose.

In general, a substance formed with considerable evolution of energy will be stable, whilst a compound formed with considerable absorption of energy will be unstable. The instability is roughly in proportion to the amount of energy absorbed in formation ; thus, perchloric acid is more stable than either hypochlorous acid or chloric acid, although hypochlorous acid is less stable than the other two. Aqueous perchloric acid is formed with considerable *evolution* of heat, and is quite stable.

The constitution of the oxy-compounds of chlorine.—If we assumed chlorine to be univalent in all its oxygen compounds, these would have the following formulæ :

chlorine monoxide, Cl—O—Cl	hypochlorous acid, H—O—Cl
chlorine dioxide, Cl—O—O—Cl	chlorous acid, H—O—O—Cl
chloric acid, H—O—O—O—Cl	perchloric acid, H—O—O—O—O—Cl

chlorine heptoxide, Cl—O—O—O—O—O—O—O—Cl

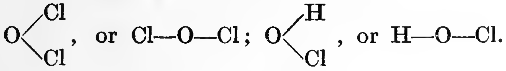
It is usually noticed, however, that the **stability** of compounds containing chains of singly-linked oxygen atoms decreases as the number of oxygen atoms in the chain increases. Thus, hydrogen peroxide, H—O—O—H, is less stable than water H—O—H. We should therefore expect the stability to decrease in the series :

$$HClO \qquad HClO_3 \qquad HClO_4$$

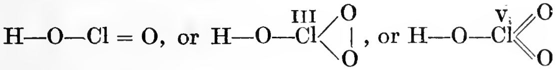
whereas it actually increases in the opposite direction.

Although the **energy-content of the molecule** is the real factor affecting stability, it is assumed that this internal energy is conditioned by the **mode of linkage of the atoms,** *i.e.*, by valency, and the formulæ of the above compounds are therefore usually written with the chlorine atom possessing different valencies, from 1 to 7 :

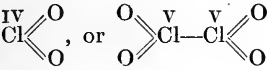
I.



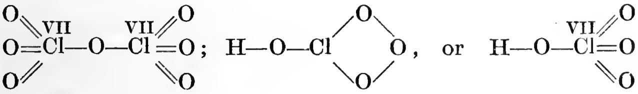
III and V.



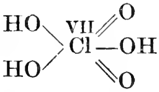
IV and V.



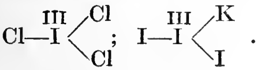
VII.



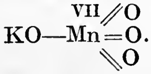
The hydrate $HClO_4,H_2O$ may be written:



The variable valency of iodine, an element very similar to chlorine and univalent in its stable compounds, is shown in the compounds ICl_3, and KI_3, in which iodine is assumed to be tervalent :



The alternative formulæ for chloric and perchloric acids, given above, are still undecided. The element manganese, which occurs in the same group of the Periodic System as chlorine, is also assumed to be heptavalent in the compound potassium permanganate, $KMnO_4$, which resembles the perchlorate in crystalline form :



EXERCISES ON CHAPTER XXI

1. What is the action of chlorine on (*a*) water, (*b*) a cold dilute solution of caustic potash, (*c*) a concentrated solution of caustic potash, (*d*) mercuric oxide, (*e*) dry slaked lime ? Give equations.

2. Starting with chlorine, caustic potash, and concentrated sulphuric acid, how would you prepare (*a*) a solution of hypochlorous acid, (*b*) chlorine monoxide, (*c*) perchloric acid, (*d*) chlorine dioxide ?

3. Describe the preparation and properties of the oxides of chlorine. What constitutional formulæ are attributed to them, and for what reasons ?

4. How are chloric and perchloric acids prepared ? How would you proceed to determine the formulæ of these acids ?

5. Describe the manufacture of bleaching powder. What is the formula of this material ? What is understood by the "Available Chlorine" of bleaching powder, and how is it estimated ?

6. What happens when a solution of bleaching powder is (*a*) heated alone, (*b*) saturated with chlorine and distilled, (*c*) heated with a little cobalt chloride solution, (*d*) added to a solution of manganous chloride ? What happens when solid bleaching powder is treated with (*a*) concentrated sulphuric acid, (*b*) hydrochloric acid ?

7. How are chlorates and perchlorates prepared on the large scale ? For what purposes are they used ? By what reactions are chlorates distinguished from perchlorates and from hypochlorites ?

8. What is the action of (*a*) concentrated hydrochloric acid, (*b*) concentrated sulphuric acid, (*c*) perchloric acid, on potassium chlorate ? Describe the action of heat on this substance.

9. A mixture of 10 c.c. of chlorine, 10 c.c. of chlorine monoxide, 10 c.c. of chlorine dioxide, and 20 c.c. of carbon dioxide is treated with caustic potash solution. What volume of gas remains ? The same mixture is then heated, and the resulting gas treated with potash solution. What are the volume and composition of the resulting gas ?

CHAPTER XXII

THE HALOGENS

BROMINE. BR = 79·29.

Bromine.—Bromine was discovered by Balard (1826) in the residues from the manufacture of solar salt (p. 220) at Montpellier. These liquors are known as **bittern,** and contain **magnesium bromide,** $MgBr_2$. On the addition of chlorine, the liquid becomes yellow, and gives an orange-red colour with starch-paste. Bromine is liberated by **displacement :** $MgBr_2 + Cl_2 = MgCl_2 + Br_2$. If the bittern is evaporated, and the residue distilled with manganese dioxide and sulphuric acid, red vapours are evolved, condensing to a nearly black liquid. This reaction suggests that the substance is similar to chlorine. The name bromine (from Greek *bromos*, a bad smell) was given to the substance on account of its unpleasant and powerful odour. Bromine was at once recognised as a **halogen,** *i.e.*, an element of the same character as chlorine ; its discovery was further evidence in favour of the elementary nature of the latter.

Bromide of silver, AgBr, occurs in certain Mexican and Chilean silver ores, but the source of the bromine of commerce is found in the magnesium, sodium, potassium, and calcium bromides of certain **mineral springs.** The Ohio springs contain 3·4–3·9 per cent. of $MgBr_2$. From these, the German springs of Kreuznach, Kissingen, and Schönebeck, and the residues of the great potash deposits of Stassfurt, practically all the bromine of commerce is made. Magnesium bromide occurs in sea-water, which contains 0·015 per cent. of bromine ; the Dead Sea and the Great Salt Lake of Utah contain considerable quantities of bromides. Bromides also occur in the Northwich brine. Bromine is found in sea animals and plants ; the ancient Tyrian purple, obtained from a shellfish, consists of dibromindigo.

Preparation of bromine.—The most important bromine compound in commerce is **potassium bromine,** KBr, used in photography, and in medicine as a sedative. From this, **bromine** can be obtained by heating with sulphuric acid and manganese dioxide (*cf.* chlorine) : $2KBr + MnO_2 + 3H_2SO_4 = Br_2 + 2KHSO_4 + MnSO_4 + 2H_2O$.

Expt. 160.—2·5 gm. of powdered KBr, mixed with 7 gm. of MnO_2, are distilled in a retort with 15 c.c. of H_2SO_4 mixed with 90 c.c. of water. The dark red vapour of bromine is condensed in a little water in the receiver (Fig. 199). A red solution of bromine, bromine water, is formed, and a small quantity of a nearly black liquid settles out at the bottom. This is bromine. The vapour acts violently on the mucous membranes, so that experiments with bromine should be carried out in a good draught. It also corrodes cork and indiarubber. The liquid should be kept in a well-stoppered bottle. It corrodes the skin, which should at once be washed with petroleum if it comes in contact with bromine.

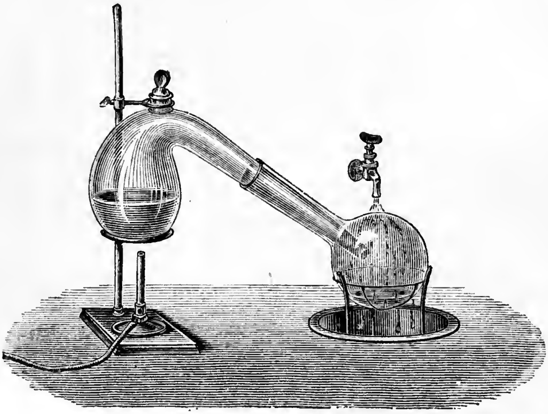


Fig. 199.—Preparation of Bromine.

Bromine may be **purified** by careful distillation. Chlorine is removed by distillation over potassium bromide: $2KBr + Cl_2 = 2KCl + Br_2$. Iodine is removed as a precipitate of cuprous iodide, CuI, by adding a solution of copper sulphate and sodium sulphite to a solution of impure potassium bromide: $2CuSO_4 + Na_2SO_3 + H_2O = Cu_2SO_4$ (cuprous sulphate) $+ Na_2SO_4 + H_2SO_4$; $Cu_2SO_4 + 2KI = 2CuI + K_2SO_4$. Scott's method of preparation of pure hydrobromic acid (p. 399) is the simplest way of obtaining a pure bromine compound.

The manufacture of bromine.—A little bromine is made from **bittern** by Balard's process. Chlorine is passed through, until the yellow colour does not increase in intensity: $MgBr_2 + Cl_2 = MgCl_2 + Br_2$. (Excess of chlorine is avoided, as it contaminates the resulting bromine.) The bromine set free is shaken out with paraffin oil, which dissolves it and floats to the surface. The oil is then shaken with a solution of caustic soda, when sodium bromide and bromate are produced, leaving the paraffin colourless and ready for use over again: $3Br_2 + 6NaOH = 5NaBr + NaBrO_3 + 3H_2O$. The aqueous layer is evaporated, heated to decompose the bromate, and distilled with manganese dioxide and sulphuric acid.

Most of the bromine sold is prepared from residual liquors, containing magnesium bromide, from Stassfurt, or Ohio. These are decomposed by chlorine in the apparatus shown in Fig. 200.

The liquor trickles down the tower, *A*, which is filled with earthenware balls, and runs into a tank, *B*, provided with perforated shelves. Steam is blown in at the bottom of this tank, and chlorine gas from the generator, *D*, passes over the surface of the liquid, and up the tower, meeting the descending liquid. The bromine is driven off by the heat of the steam, and the vapour passes out of the top of the tower to a cooling worm, where it is condensed, the last traces of vapour being kept back by moist iron filings in a small tower, *C*. The bromide of iron, Fe_3Br_8, so produced, is used as a source of potassium bromide: the solution is precipitated with potassium carbonate: $Fe_3Br_8+4K_2CO_3+4H_2O=8KBr+Fe_3(OH)_8$ (black precipitate) $+ 4CO_2$.

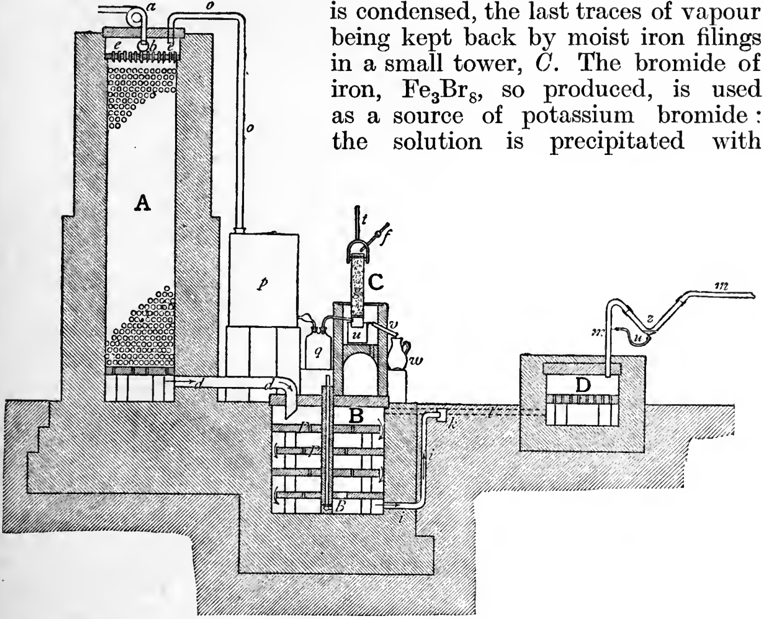


FIG. 200.—Manufacture of Bromine.

Electrolytic methods have been used, but not to any great extent.

Properties of bromine.—Bromine is a dark red, almost black, **liquid**, of high density (3·188 at 0° and 3·119 at 20°), which gives off a dark red poisonous vapour, of most irritating odour. It freezes to a dark red solid, melting at – 7·3°; at – 252° this is colourless; the boiling point is 59°. The vapour density at 100° is 85 (H = 1); at 228° it is 79·6, corresponding with the formula Br_2. At lower temperatures there may be some polymerised molecules present: $Br_4 \rightleftharpoons 2Br_2$. At 1050° dissociation into atoms to the extent of 6·3 per cent., and 30 per cent. at 1500°, occurs: $Br_2 \rightleftharpoons 2Br$. Bromine is a powerful irritant poison. It is used to some extent as a disinfectant, for which purpose it is absorbed in sticks of diatomite brick, and the product (75 per cent. Br_2) is called *solid bromine*. Bromine is also used in synthetic organic chemistry, *e.g.*, in the preparation of eosin.

Bromine combines directly with many elements, forming bromides.

Expt. 161.—Five c.c. of bromine are poured into a test-glass standing inside a wide jar, open at both ends, over a draught-hole in the bench. The top of the jar is closed by a glass plate having a small hole in the centre (Fig. 201). A *small* piece of white phosphorus thrown into the liquid causes an explosion, and is projected from the liquid. Red phosphorus burns quietly with a lurid red flame, forming yellow fumes of the pentabromide, PBr_5. Powdered arsenic burns with a reddish-white flame, forming fumes of $AsBr_3$. A *small* piece of potassium combines explosively, forming KBr. Sodium, however, does not combine with bromine unless heated to 200° in the vapour, or when water is added.

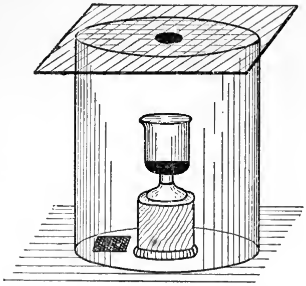


Fig. 201.—Reactions with Bromine.

Bromine vapour bleaches moist litmus paper, though more slowly than chlorine. Starch-paste is coloured orange-yellow by bromine water or vapour. **Bromine water** is a solution in water; 3·6 parts of bromine dissolve in 100 of water at 20°; the solubility decreases slowly with rise of temperature. The red solution loses bromine on exposure to air. The freezing point shows that the bromine in solution has the formula Br_2. Bromine water is stable in the dark, but decomposes in bright sunlight: $2Br_2 + 2H_2O = 4HBr + O_2$.

If saturated bromine water is cooled in a freezing mixture, red solid **bromine hydrate**, $Br_2,8H_2O$, separates. This decomposes at 17° into bromine water and bromine.

Chloroform, benzene, and carbon disulphide abstract bromine from its aqueous solution, forming orange-red liquids.

Expt. 162.—Add a little chlorine water to a solution of KBr, and shake with chloroform. The latter separates out, containing most of the bromine as a red solution. Shake this with caustic soda solution. The chloroform becomes colourless, and the aqueous layer contains bromide and bromate.

The **atomic weight** of bromine was found by Stas from the ratios $AgBrO_3 : AgBr$, and $Ag : AgBr$. Baxter (1906) synthesised AgBr, and found Ag : AgBr = 0·574453 : 1. The conversion of AgCl into AgBr gave AgBr : AgCl = 1·310171 : 1. These results agree with Stas's values. The most accurate value has been found from the density of hydrobromic acid, *i.e.*, direct to H = 1, by Moles (1916). The density of HBr at S.T.P. is 3·64442, and, after correction for deviations from Boyle's law, this gives Br = 79·29.

Hydrobromic acid, HBr.—Bromine unites directly with hydrogen when a mixture of the latter with bromine vapour is passed over heated platinum : $H_2 + Br_2 = 2HBr$. The combination is not attended with explosion, as in the case of hydrochloric acid, and does not begin in the absence of a catalyst, even in bright sunlight, below 300°. In the presence of platinum, combination begins at 200°. The heat of formation of HBr is only 12 kg. cal., as compared with 22 kgm. cal. with HCl, or 58 kg. cal. with H_2O.

EXPT. 163.—A current of dry hydrogen is passed through bromine in a wash-bottle standing in water at 60°, and the mixed gas passed over a heated spiral of platinum wire in a glass tube (Fig. 202). White fumes are produced when the gas issues into moist air. If passed into water, as shown, the gas is rapidly absorbed, forming a solution of hydrobromic acid.

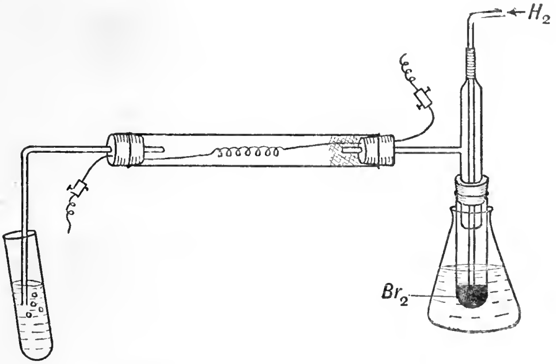


FIG. 202.—Synthesis of Hydrobromic Acid.

Hydrobromic acid is also decomposed when passed over heated platinum ; a state of equilibrium is set up : $2HBr \rightleftharpoons H_2 + Br_2$. An excess of hydrogen is used in the above experiment, when combination is nearly complete.

Hydrobromic acid is most conveniently prepared by the action of bromine on a mixture of red phosphorus and water. Phosphorus tribromide and pentabromide are probably first formed, and at once decomposed by water : $PBr_3 + 3H_2O = H_3PO_3$ (phosphorous acid) $+ 3HBr$; $PBr_5 + 4H_2O = H_3PO_4$ (phosphoric acid) $+ 5HBr$.

EXPT. 164.—Twenty gm. of red phosphorus and 40 c.c. of water are placed in a flask, and bromine is added drop by drop from a dropping funnel (Fig. 203). The gas is passed through a U-tube loosely filled with broken glass smeared with red phosphorus made into a paste with water. This removes unchanged bromine which volatilises. The addition of the first few drops of bromine is attended by lambent green flames, but when the air is displaced these disappear. The gas is collected by downward displacement in dry gas jars. The jar is full when dense fumes escape from the mouth, which is partially covered with a glass plate. The gas may also be collected over mercury (*cf.* hydriodic acid, p. 408). Commercial red phosphorus may contain arsenic, and the HBr is then contaminated with $AsBr_3$.

Hydrogen bromide may be obtained by the action of bromine on benzene: $C_6H_6 + 2Br_2 = C_6H_4Br_2$ (dibromobenzene) $+ 2HBr$. This is a reaction of **substitution** (p. 275); two atoms of hydrogen are removed from the benzene molecule, and their place is taken by two atoms of bromine. The two atoms of hydrogen form two molecules of hydrogen bromide with two other atoms of bromine from the two molecules of bromine which took part in the reaction. The molecules of the halogen are therefore divided into two parts; one enters the compound, and the other combines with the hydrogen atom which is displaced.

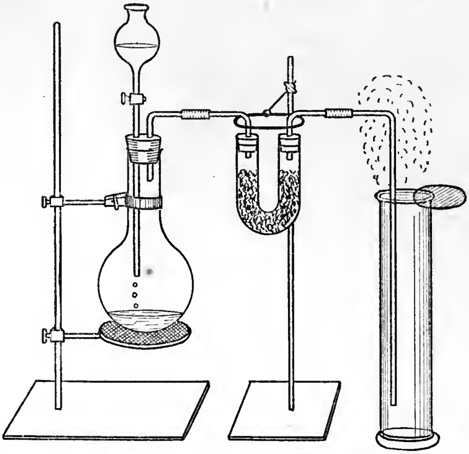


FIG. 203.—Preparation of Hydrobromic Acid.

Sixty-five c.c. of bromine are dropped slowly into 50 gm. of dry benzene mixed with a little aluminium powder in a flask. The reaction is started by gentle warming, but when evolution of gas commences the flask is cooled. The gas is scrubbed in two U-tubes, the first containing iron bromide, to remove Br_2 vapour, and the second anthracene, to remove benzene.

The **physical properties of hydrogen bromide** are as follows:

Melting point $-86°$	Density of liquid at b.-pt. 2·160
Boiling point $-68·7°$	Relative density of gas (H = 1) 40·1
Critical temperature $+91·3°$	The three forms are colourless.
Normal density 3·644 gm. per lit.	

Hydrogen bromide is very soluble in water; 1 vol. of water dissolves 600 vols. of HBr at 10°. The solution is a strong acid: $HBr \rightleftharpoons H^{\cdot} + Br'$.

EXPT. 165.—Collect a jar of the gas containing a glass bulb of water, and fitted with stopcocks as shown in Fig. 204. Break the bulb by shaking. Notice the fumes produced by the gas on contact with aqueous vapour. Dip the vertical tube under water coloured with blue litmus, and open the stopcock. The water rushes into the jar to fill the partial vacuum created by the solution of the gas, and the litmus turns red. The solution saturated at 0° contains 82, that at 15° 50, per cent. of HBr.

Aqueous hydrobromic acid may be prepared by passing the gas into water. To prevent water being forced back into the generating flask, on account of the great solubility of the gas, the latter may be passed into the water through an inverted retort, as shown in Fig. 205. If liquid is driven back, it merely collects in the bulb of the retort.

Although concentrated sulphuric acid decomposes potassium bromide with the formation of hydrobromic acid in the first instance, the gas soon becomes mixed with bromine vapour, on account of the oxidation of the hydrobromic acid by the sulphuric acid: $2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$. If, however, 0·2 gm. of stannous chloride and 3·4 c.c. of sulphuric acid are added to 25 c.c. of a solution of 15 gm. of KBr and the mixture distilled; or if KBr is distilled with syrupy phosphoric acid; a solution of hydrobromic acid, free from bromine, is obtained.

A solution of the acid is also obtained by passing sulphuretted hydrogen or sulphur dioxide through bromine covered with a layer of water: $Br_2 + H_2S = 2HBr + S$; $SO_2 + Br_2 + 2H_2O \rightleftharpoons H_2SO_4 + 2HBr$. The latter method gives pure HBr (Scott, 1900).

Three hundred and fifty c.c. of bromine are covered with 2 litres of water in a flask, and a current of SO_2 from a siphon of liquid SO_2 passed into the water through a tube ending just above the surface of the bromine, until the whole is converted into a pale yellow homogeneous liquid, which is distilled. The liquid is redistilled over $BaBr_2$ to remove sulphuric acid carried over in the first distillation.

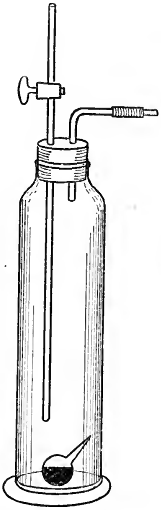


FIG. 204.—Experiment to show Solubility of Hydrobromic Acid in Water.

Concentrated hydrobromic acid fumes in moist air. On distillation it forms an acid of maximum boiling point, as in the case of hydrochloric acid (p. 237). The composition of this liquid varies from 47·38 to 47·86 per cent. HBr, according as the pressure during distillation varies from 752 to 762 mm.; it is not a definite hydrate. The boiling point under 760 mm. is 126°.

On cooling, two solid hydrates, $HBr,2H_2O$, m.-pt. $-11 \cdot 3°$, and $HBr,4H_2O$, m.-pt. $-55 \cdot 8°$, are formed. A hydrate, HBr,H_2O, has also been described.

Aqueous hydrobromic acid is decomposed by oxygen in sunlight, and becomes yellow from liberation of bromine: $4HBr + O_2 = 2H_2O + 2Br_2$. A mixture of dry HBr and oxygen is not decomposed on exposure to light. The gas or solution is decomposed by chlorine: $2HBr + Cl_2 = 2HCl + Br_2$.

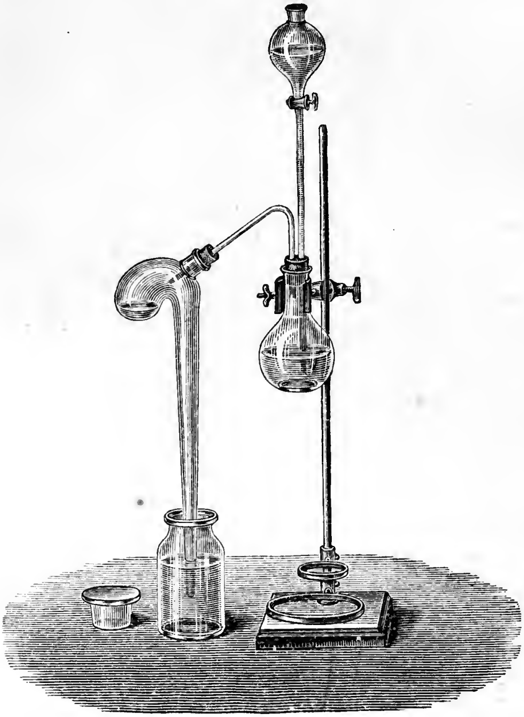


FIG. 205.—Preparation of Aqueous Hydrobromic Acid.

Bromides. — Hydrobromic acid is extensively ionised in solution, and is almost as strong as hydrochloric acid: $HBr \rightleftharpoons H^{\cdot} + Br'$. It dissolves zinc, iron, and many other metals with evolution of hydrogen, forming **bromides.** The latter may also be obtained by neutralising the acid with oxides, hydroxides, or carbonates, and by the direct union of the metals with bromine. They are ionised in solution: $KBr \rightleftharpoons K^{\cdot} + Br'$. The **bromide ion,** Br', is contained in the solutions. Nearly all bromides are soluble in water; silver, lead, and mercurous bromides only very sparingly. Silver nitrate solution is used as a test for bromides, *i.e.*, for the ion Br': a yellowish-white precipitate of AgBr is formed, insoluble in dilute nitric acid, and sparingly soluble in dilute ammonia (*cf.* AgCl and AgI). Palladium nitrate gives a reddish-brown precipitate of palladious bromide, $PdBr_2$. The formation of free bromine, soluble in chloroform with a red colour, by the action of chlorine water, and the formation of red fumes of bromine when the substance is heated with MnO_2 and H_2SO_4, are also characteristic reactions.

Oxy-acids of bromine.—No oxides of bromine are known, but the following oxy-acids have been described :

Hypobromous acid, $HBrO$.
Bromous acid, $HBrO_2$.
Bromic acid, $HBrO_3$.

Perbromic acid, and its salts, are unknown.

Hypobromous acid, HBrO.—By shaking bromine water with precipitated mercuric oxide, a solution of **hypobromous acid,** $HBrO$, is formed. By adding more bromine, and mercuric oxide, a solution containing 6 per cent. of $HBrO$ may be obtained : $2Br_2 + 2HgO + H_2O = 2HBrO + HgBr_2,HgO$. The liquid may be distilled in a vacuum at 40°. It is a yellow liquid, decomposing when heated : $4HBrO = 2H_2O + 2Br_2 + O_2$, and is a powerful oxidising and bleaching agent.

If bromine is dissolved in cold aqueous potash or soda, unstable **hypobromites** are formed : $Br_2 + 2NaOH = NaBr + NaBrO + H_2O$. These are used as oxidising agents and in the estimation of hydrogen peroxide (p. 340) and of urea (p. 538). When the solutions are kept, decomposition occurs, and a bromate is formed : $3NaOBr = 2NaBr + NaBrO_3$. Bromine vapour is also absorbed by dry slaked lime, forming a red powder similar to bleaching powder. This probably contains $CaOBr_2$; when distilled with dilute nitric acid, aqueous hypobromous acid passes over.

Bromous acid, $HBrO_2$.—This acid is said to be formed by the action of excess of bromine water on a concentrated solution of silver nitrate.

$$Br_2 + AgNO_3 + H_2O = HBrO + AgBr + HNO_3.$$
$$2AgNO_3 + HBrO + Br_2 + H_2O = HBrO_2 + 2AgBr + 2HNO_3.$$

Bromic acid, $HBrO_3$.—When bromine is dissolved in hot concentrated alkali a colourless solution is obtained which contains a **bromate** and a bromide :

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

Potassium bromate is much less soluble than the bromide, and the two salts may be separated by crystallisation, as in the case of the chlorate (p. 370). Potassium bromate also separates out when bromine vapour is passed into a solution of potassium carbonate which has been saturated with chlorine : $6KOCl + Br_2 = 2KBrO_3 + 4HCl + Cl_2$.

If silver nitrate is added to a solution of potassium bromate, **silver bromate,** $AgBrO_3$, is precipitated. If this is treated with bromine water, insoluble silver bromide is formed, and the filtered solution contains **bromic acid** : $5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3$. Bromic acid is also formed by passing chlorine through bromine water : $Br_2 + 5Cl_2 + 6H_2O = 2HBrO_3 + 10HCl$.

By evaporation on a water-bath, a 5 per cent. solution may be obtained. By distillation in a vacuum, a concentration of 50 per cent. is reached. More concentrated solutions give off bromine and oxygen: $4HBrO_3 = 2H_2O + 2Br_2 + 5O_2$. Bromic acid is a powerful oxidising agent:

$$2HBrO_3 + 5SO_2 + 4H_2O = Br_2 + 5H_2SO_4;$$
$$2HBrO_3 + 5H_2S = Br_2 + 6H_2O + 5S;$$
$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

The bromates are usually sparingly soluble in water. On heating, they decompose in one of two ways; perbromates are not formed:

1. $KBrO_3$, $HgBrO_3$, and $AgBrO_3$, give bromide + oxygen;
2. $Mg(BrO_3)_2$, $Zn(BrO_3)_2$, $Al(BrO_3)_3$, $Pb(BrO_3)_2$ and $Cu(BrO_3)_2$ give oxide + bromine + oxygen.

A mixture of $NaBrO_3 + 5NaBr$ is prepared by saturating concentrated caustic soda with bromine, and draining the separated crystals. To these sufficient $NaBrO_3$, prepared by electrolytic oxidation of NaBr, is added to form $NaBrO_3 + 2NaBr$, and the mixture is used, under the name of **bromine salt,** in the extraction of gold from its ores.

Barium bromate, $Ba(BrO_3)_2$, is precipitated when a slight excess of bromine is added to hot concentrated baryta water: $6Ba(OH)_2 + 6Br_2 = Ba(BrO_3)_2 + 5BaBr_2 + 6H_2O$. The bromide is soluble and remains in solution. If barium bromate is digested with dilute sulphuric acid, and the excess of the latter removed by baryta water, the filtered solution contains bromic acid.

IODINE. I = 125·91.

Iodine.—In 1812 Courtois, of Paris, discovered that the mother-liquors from which soda had been crystallised in the manufacture from **kelp,** or seaweed-ashes, gave off a violet vapour when heated with manganese dioxide and sulphuric acid. These vapours condensed to a black metallic-looking crystalline substance. The investigation of this material, called "the substance X," was begun by Gay-Lussac and simultaneously by Davy, who, by permission of Napoleon, was passing through Paris to Italy at the time. Davy published his results on December 11th, 1813, and Gay-Lussac a day later. The substance was recognised by these investigators as a new element analogous to chlorine, and received the name **iodine** (from the Greek *ioïdes,* violet-coloured) on account of the beautiful violet colour of its vapour (p. 10). They showed that it formed a hydrogen compound, **hydriodic acid,** HI, exactly analogous to hydrochloric acid.

Iodine, like chlorine and bromine, occurs only in combination. (Free iodine is said to exist in the water of Woodhall Spa, near Lincoln, North America.) Its compounds with metals, called

iodides, occur, in small amounts but widely diffused, in the three kingdoms of Nature. The iodine content of sea-water, which exists partly as organic compounds and partly as iodides, is small. It never exceeds 0·001 per cent., and in the Atlantic is only 1 part in 280 millions. Seaweeds and sponges absorb this iodine in the form of organic compounds (*e.g.*, iodospongin): tropical sponges may contain as much as 10 per cent. of iodine, whilst Turkey sponges contain about 0·2 per cent. The amount of iodine is greater in deep-sea weeds than in those growing near the shore. During storms, these weeds are torn up and cast ashore. They are known in Scotland as *drift-weeds*, or *red wracks*; the varieties known as *Laminaria digitata* and *L. stenophylla* alone are used in the manufacture of iodine.

The weeds are burnt in shallow pits, and the ashes, known as **kelp** (**varec** in Normandy), contain potassium salts and from 0·4 to 1·3 per cent. of iodine as iodides. Formerly, in Normandy, Spain, and Scotland, these ashes were used in the manufacture of alkali (potash); the manufacture of iodine was begun by Dr. Ure at Glasgow, and three works are still in operation in that town. Iodine manufacture is also carried out from seaweed in Norway and Japan.

Iodine occurs in oysters and many sea-animals. It is present in traces in cod-liver oil, as an organic compound, and occurs as an organic compound **iodothyrin,** $C_{11}H_{10}O_3NI_3$, in the thyroid glands (especially of the ray and dogfish, which contain 1 per cent. of iodine). In the mineral kingdom iodine occurs in certain lead and silver ores, and in some magnesian limestones and dolomites. The deposits of seaweed in strata in Central Europe contain iodine, and the water which percolates to them appears in springs which contain iodides, such as those of Heilbrunn, and of Montpellier, which are used medicinally.

The iodine of the body seems to be absorbed in the lungs from the spores of lower organisms floating in the air; normally about 0·005 mgm. of I passes into the lungs in this way per twenty-four hours.

The most important source of iodine is the sodium iodate contained, to the extent of 0·2 per cent., in crude Chile nitre (*caliche*). The mother-liquors from the crystallisation of the nitrate contain about 3 gm. of iodine as iodate per litre.

Preparation of iodine.—In the laboratory, iodine may be obtained by heating potassium iodide with sulphuric acid and manganese dioxide: $2KI + MnO_2 + 3H_2SO_4 = I_2 + 2KHSO_4 + MnSO_4 + 2H_2O$.

EXPT. 166.—Heat 3·5 gm. of KI with 7 gm. of MnO_2 and 100 c.c. of dilute H_2SO_4 (1 : 6) in a retort. Beautiful violet vapours are given off, which condense in the neck of the retort and in the receiver as glittering black scales of solid iodine.

In the manufacture of iodine the kelp is lixiviated with water in iron vats, heated by steam, and the solution concentrated in iron pans. The salts which separate, called *plate sulphate*, consisting chiefly of potassium sulphate, are fished out. On cooling, impure potassium chloride separates, and on further evaporation crude sodium chloride (" kelp salt ") is deposited. The final mother-liquor contains the very soluble sodium and potassium iodides, together with some bromides. It is mixed with sulphuric acid, and the sulphur, from the decomposition of sulphides, allowed to settle. The clear liquor is then run into the iodine stills, consisting of iron pots with dome-shaped lead covers communicating with trains of earthenware receivers, called *udells* (Fig. 206). Manganese dioxide is added, and iodine distils off on heating, collecting in the udells. It is purified by sublimation in porcelain pans. About 12 lb. of iodine are obtained per ton of kelp, representing about half that contained in the original weed.

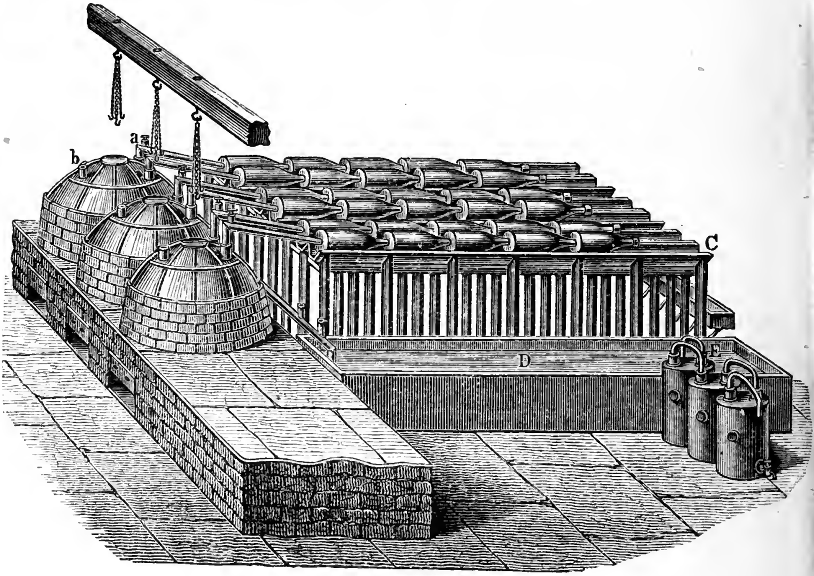


FIG. 206.—Manufacture of Iodine.

The two processes of Stanford (1863), established in the Outer Hebrides, are no longer worked. In the **char process,** the sun-dried weed was distilled in iron retorts at a low red heat. It was expected that acetic acid and tar would be recovered, but only a little evil-smelling tarry water came over. The residue was lixiviated. In the **wet process,** the weed was boiled with sodium carbonate solution.

and filtered. Fairly pure cellulose, amounting to 15 per cent. of the weed, was left. This was called *algulose*, and was used for making paper. On acidifying the filtrate, a gelatinous substance called *algin* was thrown down, which was used in making jellies, sizing paper, and as a glue. The filtrate, containing iodides, was evaporated, neutralised with limestone, and distilled with sulphuric acid and manganese dioxide. This process seems to have been recently revived in Norway; the algin is sold as *Norgine* for use as an adhesive.

In France, the kelp liquors are acidified with hydrochloric acid, and chlorine is passed in. Iodine is precipitated; it is filtered off, washed, dried, and resublimed in earthenware retorts: $2KI + Cl_2 = 2KCl + I_2$.

The main source of iodine at the present day is the mother-liquor (" aqua vieja ") of **caliche.** This contains about 4·5 gm. of **sodium iodate,** $NaIO_3$, per litre. It is run into lead-lined vats, and treated with dilute sulphuric acid and sodium hydrogen sulphite. **Iodic acid** is first liberated, and is then reduced by sulphurous acid:

$$(1)\ NaIO_3 + H_2SO_4 = NaHSO_4 + HIO_3.$$
$$(2)\ 2HIO_3 + 5H_2SO_3 = I_2 + 5H_2SO_4 + H_2O.$$

The liberated iodine at first reacts with the excess of sulphurous acid, and it is only at the end of the reaction, when the latter is used up, that iodine appears:

$$(3)\ I_2 + H_2O + H_2SO_3 = 2HI + H_2SO_4.$$
$$(4)\ HIO_3 + 5HI = 3H_2O + 3I_2.$$

The iodine precipitated is pressed, washed, and resublimed.

The above process involves the mutual decomposition of iodic acid and hydriodic acid: the former is an oxidising agent and the latter a reducing agent. This reaction sets in only when all the free sulphurous acid is used up, and the whole process therefore exhibits a **period of induction** (p. 235). This is very clearly shown in the following experiment, due to Landolt.

EXPT. 167.—Dissolve 10 gm. of crystallised iodic acid in 1 litre of water. Saturate 5 c.c. of water with sulphur dioxide, and add the solution to 1 litre of water. 50 c.c. of the iodic acid solution are added to 250 c.c. of water in a cylinder, and a little starch solution is added. 50 c.c. of the sulphurous acid are diluted with 250 c.c. of water in a cylinder, and the solution is poured quickly into the iodic acid. The liquid remains colourless for a certain interval, and then at once becomes blue. By varying the dilution, the time interval may be altered. This is an example of **successive reactions**; the later reactions use up the products of the first, and the speed of the whole reaction is that of the slowest component reaction.

Pure iodine.—Commercial iodine nearly always contains **iodine chloride,** ICl, **iodine bromide,** IBr, and sometimes **cyanogen iodide,** ICN. All these substances are volatile, and cannot be separated by sublimation. Resublimation over potassium iodide removes most of the impurity.

EXPT. 168.—A little iodine is ground up in a mortar with potassium iodide, and the mixture gently heated in a porcelain dish on a sand-bath. A larger porcelain dish, filled with cold water, is placed over the first one, and the purified iodine condenses on its under surface in glittering scales with a brilliant metallic lustre.

Stas dissolved resublimed iodine in a strong solution of KI, precipitated it with water, and distilled it in steam. The solid iodine which came over was collected, dried *in vacuo* over solid calcium nitrate (frequently renewed), and finally sublimed over caustic baryta, BaO, to separate HI and H_2O. Ladenburg (1902) washed precipitated silver iodide with dilute ammonia to free it from chloride, reduced it with zinc and dilute sulphuric acid, $AgI + H = Ag + HI$, precipitated the iodine from the solution with nitrous acid: $2HI + 2HNO_2 = 2H_2O + 2NO + I_2$, distilled it in steam, and dried it over calcium chloride. Lean and Whatmough (1900) heated pure cuprous iodide to 240° in a current of dry air: $Cu_2I_2 + O_2 = 2CuO + I_2$.

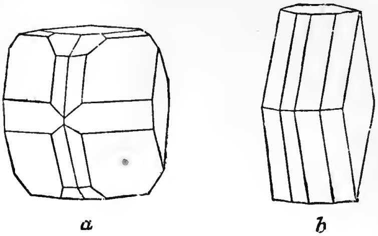


FIG. 207.—Crystals of Iodine.

Properties of iodine.—Iodine is a blackish-grey crystalline solid which is opaque, and has almost a metallic lustre. (When deposited in thin films on glass at −180° it is transparent.) Large crystals, belonging to the rhombic system (Fig. 207), are produced by the spontaneous evaporation of the ethereal solution, or by allowing hydriodic acid to oxidise by exposure to air. The **physical properties of iodine** have been differently stated:

	Stas :—	Ladenburg :—
Sp. gr.	4·948 (17°).	4·933 (4°/4°)
Melting point	114·2° (solidif. at 113·6°).	116·1°
Boiling point	184·35° (Ramsay and Young).	183·05°.

Iodine vapour when pure has a splendid deep-blue colour; when mixed with air it is reddish-violet (Stas).

The **density of iodine vapour** diminishes with rise of temperature. At the boiling point it corresponds with the formula I_2; this remains practically constant up to 700°, but then diminishes up to 1700°, when it again becomes constant and corresponds with the formula I. The dissociation into atoms: $I_2 \rightleftharpoons 2I$, which is doubtful in the case of chlorine and bromine, is therefore well established with iodine.

Iodine vapour shows an orange-yellow **fluorescence,** especially when exposed to green rays. When exposed to the light from a mercury lamp, it emits a complicated **resonance spectrum,** consisting of a large number of equally-spaced lines.

Iodine is much less soluble in water than either chlorine or bromine; 1 part dissolves in 3616 of water at 18°, 2145 parts at 35°, and 1084 parts at 55°. The solution has a brownish-yellow colour, and appears to undergo slight decomposition on standing: $2I_2 + 2H_2O \rightleftharpoons 4HI + O_2$. For this reason the solubility of iodine slowly increases, since the element is readily soluble in solutions of hydriodic acid or iodides, forming dark brown liquids containing the ion I_3'. From the solution in potassium iodide, black crystals of **potassium tri-iodide,** KI_3, may be obtained. Chloroform and carbon disulphide, which readily extract iodine from aqueous solutions, forming purple solutions, do not do so from solutions in potassium iodide. The compounds CsI_3, CsI_5, RbI_3, and KI_7 are known.

Iodine is readily soluble in alcohol, forming a brown solution known as **tincture of iodine** ($\frac{1}{2}$ oz. of iodine + $\frac{1}{4}$ oz. of potassium iodide + 1 pint of rectified spirit). The solution in ether is also brown, and it is suggested that in these solutions the iodine is in combination with the solvent. The depression of freezing point of methylene iodide, CH_2I_2, containing dissolved iodine, gives the formula I_2.

Iodine combines directly with many elements, such as phosphorus (p. 18), and mercury (p. 116), forming **iodides.**

Test for iodine.—Solutions of iodine give a beautiful blue colour with starch-paste. The latter is prepared by boiling "soluble starch" with water, or adding boiling water to ordinary starch made into a paste with cold water. 1 part of iodine in 450,000 parts of water may be detected by this reaction. The blue colour disappears on heating, but reappears on cooling.

EXPT. 169.—Add a drop of iodine solution to some starch solution in a test-tube. Dip the lower part of the tube containing the blue liquid into a beaker of boiling water: the lower part becomes colourless. Cool under the tap; the whole again becomes blue. If excess of chlorine water is added, the blue colour again disappears, since iodine chloride, ICl, is formed.

The blue substance has been variously supposed to be a chemical compound—"iodide of starch"—or a solid solution, or an adsorption complex of starch and iodine. A blue colour is produced by the action of iodine on other substances, *e.g.*, saponarin, some of which are crystalline, and it appears only in the presence of iodides, or electrolytes. Basic lanthanum and praseodymium acetates, which are colloidal, also give a blue colour with iodine.

Hydriodic acid, HI.—Hydrogen and iodine combine only with a very feeble affinity. The affinity for hydrogen diminishes very rapidly in the series: Cl, Br, I. A mixture of iodine vapour and hydrogen passed over heated spongy platinum forms **hydrogen iodide,** HI, giving fumes in moist air, but the reaction is reversible and incomplete: $H_2 + I_2 \rightleftharpoons 2HI$.

Hydriodic acid may be obtained by heating potassium iodide with phosphoric acid; with sulphuric acid oxidation occurs, iodine being set free, and the sulphuric acid is reduced to sulphuretted hydrogen (*cf.* HBr): $H_2SO_4 + 8HI = H_2S + 4H_2O + 4I_2$. The usual method of preparation is by the action of water on a mixture of red phosphorus and iodine: $2P + 5I_2 + 8H_2O = 10HI + 2H_3PO_4$. Phosphorus iodides are probably first formed, and then decomposed by water, as in the preparation of hydrobromic acid.

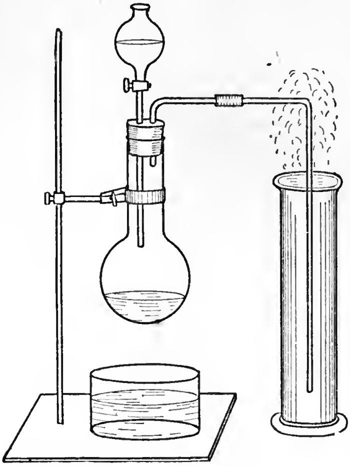


FIG. 208.—Preparation of Hydrogen Iodide.

EXPT. 170.—Four gm. of red phosphorus and 20 gm. of iodine are shaken together in a flask, and water is slowly dropped on the mixture from a tap-funnel (about 15 c.c.). The evolution of gas may become very rapid, and the flask is then cooled. The gas is collected directly by displacement (Fig. 208). It is very soluble in water, and attacks mercury.

Hydrogen iodide is a colourless gas, very soluble in water (425 vols. HI in 1 vol. at 10°), and fuming strongly in moist air. The solubility may be demonstrated by EXPT. 165. The gas condenses to a liquid under 4 atm. pressure at 0°, and is therefore much more easily liquefied than HCl or HBr. The **physical properties** of HI are as follows:

Boiling point	− 35·5°	Relative density (H = 1) 63·94
Melting point	− 50·9°	(theoretical for HI = 63·45)

The volumetric composition of the gas, as well as that of hydrogen bromide, may be demonstrated by the action of sodium amalgam, as in the case of hydrogen chloride. Half the volume of hydrogen remains.

A jet of hydrogen iodide may be burnt in oxygen, with liberation of violet fumes of iodine: $2HI = H_2 + I_2$; $2H_2 + O_2 = 2H_2O$.

Hydrogen iodide is decomposed by exposure to sunlight: after ten days Victor Meyer found 60 per cent. decomposed; after a year, 99 per cent.: $HI \rightleftharpoons H + I$. The decomposition is also readily brought about by heat: $2HI \rightleftharpoons H_2 + I_2$: a hot glass rod placed in a jar of the gas liberates violet fumes of iodine. The decomposition begins at 180°, but is then very slow. The rate of decomposition is quicker the higher the temperature. At each temperature a fixed amount of decomposition is ultimately reached, and then remains constant, *i.e.*, a **state of equilibrium** is attained: $2HI \rightleftharpoons H_2 + I_2$. At 350°, 17·3 per cent., at 444°, 79 per cent., of the gas is decomposed. The limit of decomposition at 250° is reached only after several months, but at 444° it is attained after a few hours. The rate of reaction is considerably accelerated by the presence of spongy platinum, which acts as a catalyst. The reverse reaction: $H_2 + I_2 \rightleftharpoons 2HI$, also proceeds slowly, but is accelerated by platinum. At 444°, the reaction stops when 21 per cent. of hydriodic acid is formed, and therefore 79 per cent. of the hydrogen and iodine vapour (in equal volumes) remains uncombined. Thus, *the same equilibrium state is attained, at a given temperature, from the mixture of hydrogen and iodine vapour* ($H_2 + I_2$) *as from hydriodic acid* ($2HI$). This is characteristic of truly **reversible reactions.** The catalyst produces no change in the composition of the equilibrium mixture, since it accelerates equally both the direct and inverse reactions.

Aqueous hydriodic acid is produced by dissolving the gas in water. The apparatus shown in Fig. 205 may be used to prevent the liquid being drawn back into the flask, owing to the great solubility of the gas.

The solution saturated at 0° has a sp. gr. of 1·99, and contains 90 per cent. of HI. The hydrate $HI,2H_2O$, m.-pt. − 43°, separates on cooling. The solution ordinarily used in organic chemistry as a **reducing agent** has a sp. gr. of 1·5.

An acid of maximum boiling point 127° at 76 cm. contains 57 per cent. of HI. The aqueous solution when freshly prepared is colourless, but rapidly becomes brown when exposed to air, owing to formation of iodine, which dissolves in the acid:

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

The ease with which this reaction occurs renders the concentrated aqueous acid a valuable **reducing agent.**

Chlorine, or bromine, water readily liberates iodine from the acid:

$$2HI + Cl_2 = 2HCl + I_2; \quad \text{or} \quad 2I' + Cl_2 = 2Cl' + I_2.$$

Aqueous hydriodic acid is also formed by passing sulphuretted hydrogen through a suspension of iodine in water:

$$H_2S + I_2 = 2HI + S;$$

the sulphur is filtered off. When the density of the solution reaches

1·56, the action ceases. Sulphuretted hydrogen gas does not act upon dry iodine, but the heat of solution of the hydrogen iodide in water supplies the energy necessary for the reaction :

$$\begin{array}{rcll} H_2S & = & H_2 + S & - \ 2{\cdot}7 \text{ kg. cal.} \\ H_2 + I_2 \text{ (solid)} & = & 2HI & - \ 12 \text{ kg. cal.} \\ \hline \therefore \quad H_2S + I_2 & = & 2HI + S & - \ 19{\cdot}7 \text{ kg. cal.} \\ \hline \end{array}$$

The heat of solution of 2HI in a large quantity of water is 38·4 kg. cal., hence the heat evolved at the beginning of the reaction is :

$$H_2S + I_2 \text{ (solid)} + \text{Aq.} = 2HI,\text{Aq.} + S + (38{\cdot}4 - 19{\cdot}7) \text{ kg. cal.}$$

As the solution becomes concentrated, the heat of solution of the hydrogen iodide becomes less, until at sp. gr. 1·56 it is only 19·7 kg. cal. for 2HI. Further action then ceases.

Although the heat of formation of hydrogen iodide from hydrogen and *solid* iodine is attended with an absorption of heat, the reaction $H_2 + I_2$ (vap.) = 2HI is attended with a slight *evolution* of heat, *i.e.*, a little heat is absorbed when hydrogen iodide dissociates into hydrogen and iodine *vapour*. The extent of dissociation therefore increases with the temperature (p. 355).

Chlorides of iodine.—Iodine monochloride is formed by passing chlorine over iodine : $I_2 + Cl_2 = 2ICl$. A dark red liquid is formed, which solidifies on standing, especially in contact with a trace of ICl_3. The first product of solidification melts at 14°, but is unstable, and is converted on standing into another stable modification, melting at 27·2°, which forms beautiful red needles. This is the stable form under *all* conditions ; from the liquid cooled below 14°, crystals of either form separate according as a crystal of one or the other form is added. The unstable form is obtained by cooling the liquid to − 10°.

Iodine monochloride is decomposed by water :

$$5ICl + 3H_2O = 5HCl + 2I_2 + HIO_3 \text{ (iodic acid) ;}$$

alkalies decompose it into chloride, iodate, and iodide. It is also formed by dissolving iodine in aqua regia, and extracting with ether, or by heating iodine with potassium chlorate. It boils at 101·3°, and the vapour density is normal.

Iodine trichloride, ICl_3, is obtained by the action of excess of chlorine on iodine, or on the monochloride : $ICl + Cl_2 \rightleftharpoons ICl_3$. The latter reaction is reversible, since the vapour density of the trichloride shows that it is dissociated ; the decomposition is complete at 670°. It may be volatilised in an atmosphere of chlorine. The trichloride is also produced by heating iodine pentoxide in hydrogen chloride: $I_2O_5 + 10HCl = 2ICl_3 + 5H_2O + 2Cl_2$. It is a lemon-yellow crystalline solid, which is decomposed by alkalies in the same way as the monochloride.

Expt. 171.—If a jar of hydrogen iodide is inverted over a similar jar of chlorine, and the glass plates are withdrawn, there is a violent reaction, and dense fumes are formed. On standing, three substances are seen to have been formed: (i) a violet vapour, depositing solid crystals of **iodine** in the upper jar; (ii) dark red drops of liquid at the junction of the two jars—this is **iodine monochloride,** ICl; (iii) lemon-yellow crystals in the lower jar—these are **iodine trichloride,** ICl_3. The reaction is:

$$4HI + 4Cl_2 = 4HCl + I_2 + ICl + ICl_3.$$

On standing, only yellow crystals of ICl_3 remain.

Iodine trichloride may be regarded as a *salt*; **iodine acetate,** $I(C_2H_3O_2)_3$, is obtained by the action of Cl_2O on iodine dissolved in glacial acetic acid, and a **sulphate,** $I_2(SO_4)_3$, and **perchlorate,** $I(ClO_4)_3,2H_2O$, have been prepared. The latter is obtained in yellowish-green needles by the action of ozone on a cooled solution of iodine in anhydrous perchloric acid: $I_2 + 6HClO_4 + O_3 = 2I(ClO_4)_3 + 3H_2O$. The strongly basic **diphenyl-iodonium hydroxide,** $(C_6H_5)_2IOH$, is stable, and forms salts which resemble those of tervalent thallium (p. 904), even to giving a green flame reaction.

A stable **pentafluoride,** IF_5, m.-pt. $-8°$, b.-pt. 97°, is formed directly from the elements, and is of interest in demonstrating the quinquevalence of iodine in some of its compounds (*cf.* iodic acid).

Oxides and oxy-acids of iodine.—The following **oxy-compounds of iodine** are known:

Oxides.	**Oxy-acids.**
—	**Hypoiodous acid,** HOI
Iodine dioxide, IO_2 or I_2O_4	—
Iodine pentoxide, I_2O_5	**Iodic acid,** HIO_3
—	**Periodic acid,** $HIO_4,2H_2O$ or H_5IO_6

A number of salts of periodic acids of different formulæ are known.

Oxides of iodine.—The best-known oxide of iodine is the pentoxide, but two lower oxides, I_4O_9 and IO_2 have been described.

A green **oxide,** I_4O_9 (p. 329), is said to be formed by the action of ozone on dry iodine. The **dioxide,** IO_2, or I_2O_4, is obtained as a lemon-yellow powder by the action of cold nitric acid on iodine, or by the action of hot concentrated sulphuric acid on iodic acid. It decomposes into its elements at 130°.

Iodine pentoxide, or **iodic anhydride,** I_2O_5, is obtained by heating iodic acid to 200° : $2HIO_3 = H_2O + I_2O_5$. It forms white scaly crystals, decomposing at 300° after fusion, into oxygen and iodine. It oxidises carbon monoxide on warming, even if this gas is contained only in traces in gaseous mixtures : $5CO + I_2O_5 = 5CO_2 + I_2$. The carbon dioxide formed may be absorbed by baryta water, and the amount determined by titration. Iodine pentoxide dissolves in water, forming **iodic acid**, HIO_3. It is the anhydride of this acid.

Hypoiodous acid, HOI.—Iodine dissolves in cold dilute alkali to form a yellow solution, with a characteristic odour of saffron. This contains free **hypoiodous acid,** HOI. Probably a hypoiodite is first formed, but this is almost completely hydrolysed by water, even in presence of excess of alkali :

$$I_2 + 2KOH \rightleftharpoons KI + KOI + H_2O.$$
$$KOI + H_2O \rightleftharpoons HOI + KOH.$$

The reaction involves the hydrolysis of the iodine molecule : $I_2 + H_2O \rightleftharpoons HI + HOI$. The compound HOI appears from this equation, and from its properties, to be a **feeble base** rather than an acid. The existence of a lower oxide of iodine in the freshly-prepared solution of iodine in alkali may be inferred from the colour and smell of the solution, and its strong oxidising and bleaching properties. Indigo solution is bleached, hydrogen peroxide evolves oxygen, manganous sulphate is precipitated as brown manganic hydroxide, $Mn(OH)_3$, and if alcohol is added to the solution a yellow precipitate of iodoform, CHI_3, is formed :

$$C_2H_5{\cdot}OH + 4I_2 + 6KOH =$$
$$CHI_3 + HCO_2K \text{ (potassium formate)} + 5KI + 5H_2O.$$

On standing, especially if heated, the alkaline solution of iodine loses all these properties, and contains only an iodide and iodate : $3KOI = KIO_3 + 2KI$. Free hypoiodous acid is also formed on shaking an aqueous solution of iodine with precipitated mercuric oxide : $2HgO + 2I_2 + H_2O = HgI_2,HgO + 2HOI$.

Iodic acid, HIO_3.—This, the most important oxy-acid of iodine, is formed by the oxidation of the latter with ozone in presence of water, or by heating iodine with ten times its weight of nitric acid (sp. gr. 1·5) in a flask on a water-bath, evaporating to dryness, heating to 200° to expel nitric acid, and dissolving the iodine pentoxide formed in the smallest amount of warm water. On cooling the syrupy liquid, colourless rhombic crystals of **iodic acid** separate.

It is also formed by passing chlorine through a suspension of iodine in water : $I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl$. Hydrochloric acid is removed by evaporation, or by addition of silver oxide, when insoluble silver chloride is formed.

Iodic acid is insoluble in alcohol, but is very soluble in water, and is deliquescent. The solution first reddens, and then bleaches litmus paper. The solid deflagrates when heated with powdered charcoal, sulphur, phosphorus, or organic matter. It is an oxidising agent :

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

If iodine is dissolved in aqueous caustic potash, an **iodate** is formed : $3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O$ (Davy, 1815). If an acid is now added, the whole of the iodine is again set free, on account of the reduction of the iodic acid by the hydriodic acid. If neutral solutions of iodate and iodide are mixed, an acid may be estimated by adding it to this solution, and titrating the iodine liberated.

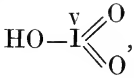
If iodine is added to a hot concentrated solution of potash, **potassium iodate,** KIO_3, crystallises out on cooling, as it is sparingly soluble. The salt may also be prepared by heating iodine with potassium chlorate, or by adding iodine to a hot concentrated solution of potassium chlorate, and boiling with a few drops of nitric acid. Chlorine is expelled : $2KClO_3 + I_2 = 2KIO_3 + Cl_2$. If barium chloride is added to a solution of potassium iodate, **barium iodate** is precipitated. This is decomposed by dilute sulphuric acid, forming iodic acid : $Ba(IO_3)_2 + H_2SO_4 = BaSO_4 + 2HIO_3$.

Iodic acid forms three series of salts, viz., normal salts and two acid salts :

Normal potassium iodate, KIO_3 ;
Acid potassium iodate, KIO_3,HIO_3, or KHI_2O_6 ;
Diacid potassium iodate, $KIO_3,2HIO_3$.

The acid salts are isomorphous with acid salts of some dibasic organic acids (succinic, etc.), so that the acid is sometimes regarded as dibasic, $H_2I_2O_6$. The normal iodates are insoluble, or sparingly soluble, in water. On heating, they break up in one of two ways : (i) into iodide + oxygen ; (ii) into oxide + iodine + oxygen. Barium iodate forms a **periodate** (see below). Iodates form complex compounds with molybdic, tungstic, and phosphoric acids, and with selenates.

Iodates are detected by the blue colour, due to liberation of iodine, produced when sulphur dioxide is passed through the solution, to which starch-paste has been added.

The formula of iodic acid is assumed to be  $HO-\overset{v}{I}\genfrac{}{}{0pt}{}{=O}{=O}$, in which iodine is quinquevalent. This does not, however, explain the formation of the acid salts.

Periodic acid, $HIO_4,2H_2O$, or H_5IO_6.—If a concentrated solution of iodic acid is electrolysed at low temperatures, with a lead plate covered with lead peroxide as anode, enclosed in a porous cell, and a platinum plate immersed in dilute sulphuric acid as a cathode outside, it is oxidised to **periodic acid,** HIO_4. The solution yields colourless, deliquescent crystals, of the formula $HIO_4,2H_2O$. The anhydrous acid is not known, and the water cannot be removed from the acid without decomposing the latter, so that the formula is probably H_5IO_6, salts of which are known. The crystals melt at 133°, and decompose at 140°: $2H_5IO_6 = I_2O_5 + 5H_2O + O_2$.

The solution is strongly acid, and is an oxidising agent, but it does not oxidise sulphur dioxide.

If a solution of potassium iodate, to which a little potassium chromate has been added, is electrolysed as described, sparingly soluble **potassium periodate,** KIO_4, is formed. An **acid sodium periodate,** $Na_2H_3IO_6$, is formed by oxidising a boiling solution of 13 gm. of iodine, in a 10 per cent. solution of 60 gm. of caustic soda, with a rapid stream of chlorine. The salt is precipitated. A solution of this salt gives with silver nitrate a black precipitate of the silver salt, Ag_3IO_5, which is decomposed by chlorine in presence of water, giving silver chloride and a solution of periodic acid.

Barium periodate, $Ba_5(IO_6)_2$, is very stable, and is formed on heating barium iodate to redness:

$$5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4I_2 + 9O_2.$$

It is decomposed by dilute sulphuric acid, with formation of periodic acid.

The **periodates** appear to be derived from acids formed by the addition of water to a hypothetical anhydride, I_2O_7, in which iodine is septavalent:

$I_2O_7 + H_2O = 2HIO_4$, forming **meta-periodates,** *e.g.*, KIO_4, $AgIO_4$;
$I_2O_7 + 2H_2O = H_4I_2O_9$, forming **diperiodates,** *e.g.*, $Na_4I_2O_9$;
$I_2O_7 + 3H_2O = 2H_3IO_5$, forming **mesoperiodates,** *e.g.*, Ag_3IO_5;
$I_2O_7 + 5H_2O = 2H_5IO_6$, free **paraperiodic acid,** forming, *e.g.*, $Ba_5(IO_6)_2$.

The atomic weight of iodine.—The atomic weight of iodine is of considerable theoretical importance in connection with that of tellurium (p. 533), and several exact determinations of its value have been made. Stas determined the ratio AgI : O by decomposing silver iodate by heat, and absorbing the oxygen in red-hot copper. He also determined the ratio Ag : AgI = 100 : 217·534, which, with the value 107·94 (O = 16) for silver, gave I = 126·86 (O = 16). This value, agreeing exactly with that of Marignac, determined by the same method, was later found to be about half a part per thousand too small, by reason of the occlusion of silver nitrate in the precipitated silver iodide. More recent determinations, all based on the value for silver, give I = 126·92 (O = 16), or 125·91 (H = 1).

FLUORINE. F = 18·9.

Fluorine.—The mineral *fluorite*, or *fluorspar*, occurs in Derbyshire, crystallised in cubes or octahedra (Fig. 209), or in compact masses, like marble. It is known as "Derbyshire Spar," or, when coloured blue or purple, as "Blue John." Colourless, transparent crystals exhibit a bluish tinge when light falls on them, and this property, which is shown by petroleum, solutions of quinine salts, and other substances, is therefore known as **fluorescence** (*cf.* p. 8). Fluorspar occurs in many other localities, and has long been used in metallurgy as a **flux,** *i.e.*, a substance which forms with the earthy portions of ores (*gangue*) a readily fusible slag, which flows away from the metallic part on reduction, leaving the metal as a separate layer. For this reason the mineral obtained its name, from the Latin *fluo*, I flow.

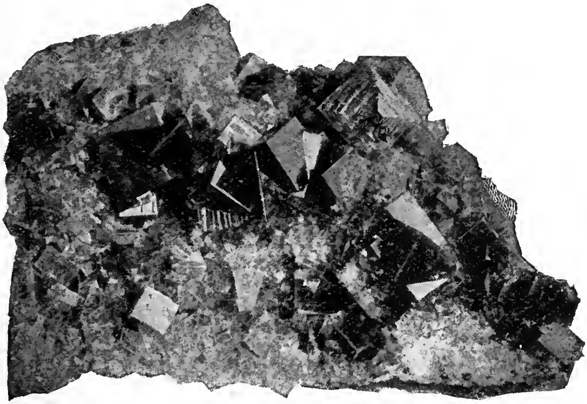


FIG. 209.—Crystals of Fluorspar.

The composition of fluorspar was for a long time unknown. About 1670, Schwankhardt, of Nuremberg, observed that a mixture of powdered fluorspar and concentrated sulphuric acid corroded glass, and in 1771 Scheele discovered that the mineral was a salt of lime and a peculiar acid, which he obtained in an impure state by distilling fluorspar with concentrated sulphuric acid in a tin retort. A glass retort was powerfully corroded, and a gas formed which deposited gelatinous silica on passing into water. Gay-Lussac and Thenard investigated the acid in 1809; they regarded it as the oxide of an unknown radical. Ampère, in 1810, suggested that it was probably a compound of hydrogen with an unknown element, **fluorine,** analogous to hydrochloric acid. Fluorspar would then be calcium fluoride, CaF_2. The element was first isolated by Moissan in 1886.

Fluorine is widely distributed in Nature, both in the form of fluorspar and in other fluorides. Large quantities of *cryolite*, a double fluoride of sodium and aluminium, $AlF_3,3NaF$, are found in

Greenland, and *fluor-apatite*, $CaF_2,3Ca_3(PO_4)_2$, is a common mineral. Small quantities of calcium fluoride in the soil, probably derived from apatite, are absorbed by plants, the ashes of which contain about 0·1 per cent. of fluorine. From plants, calcium fluoride passes into the bones and teeth of animals, especially into the hard parts; the enamel of teeth may contain 0·3 per cent. of fluorine, possibly in combination as apatite.

Traces of free fluorine seem to occur in varieties of fluorspar, such as that of Wölsendorf, which have been decomposed by the radioactive uranium minerals found in the same localities. The blue colour of some kinds of fluorspar is apparently due to organic matter. On heating, the blue colour disappears. Colourless fluorspar also becomes blue when exposed to radium emanation.

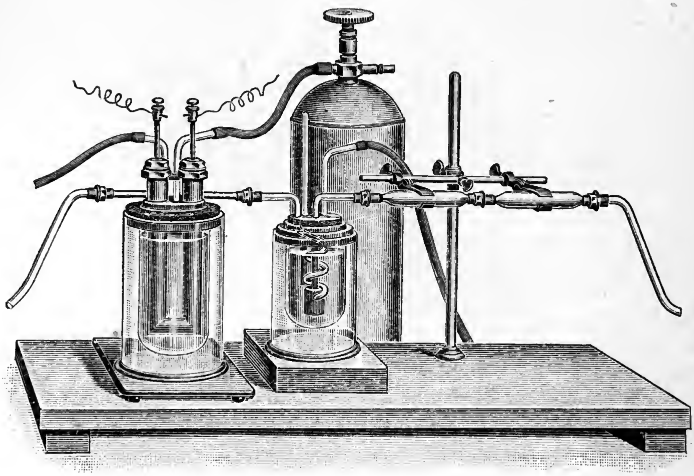


FIG. 210.—Moissan's Apparatus for Preparing Fluorine.

The isolation of fluorine.—The isolation of fluorine was for a long time one of the master problems of inorganic chemistry. The attempts of Davy, Fremy, Nicklès, Louyet, and Gore were uniformly unsuccessful. On account of the exceedingly poisonous and corrosive character of anhydrous hydrofluoric acid, which was involved in the experiments, more than one chemist lost his life. If platinum vessels were used, a chocolate-coloured powder, PtF_4, was obtained, and carbon vessels were attacked, with the formation of a gaseous fluoride, CF_4. Attempts to electrolyse hydrofluoric acid met with no success; if the aqueous acid was used, only oxygen and hydrogen were obtained, whilst the anhydrous acid is a non-conductor of electricity.

It was not until 1886 that Moissan, after a long series of unsuccessful attempts, was able to bring free fluorine to the light of day; his triumph was the culmination of a long, dangerous, and expensive research. Moissan's success dated from his discovery that anhydrous hydrofluoric acid, although an insulator, became an electrolyte when potassium hydrogen fluoride, KHF_2, was dissolved in it. If this solution was electrolysed in a **U**-tube composed of an alloy of platinum and iridium, with electrodes of the same material, the whole being strongly cooled to minimise the corrosive action of the electrolyte, then hydrogen was evolved from the cathode, and the long-sought element **fluorine** was given off from the anode as a gas. In 1899 Moissan found that the expensive platinum apparatus could be replaced by one of copper, which apparently becomes coated with a protecting film of fluoride. The electrodes, however, must still be of platinum-iridium.

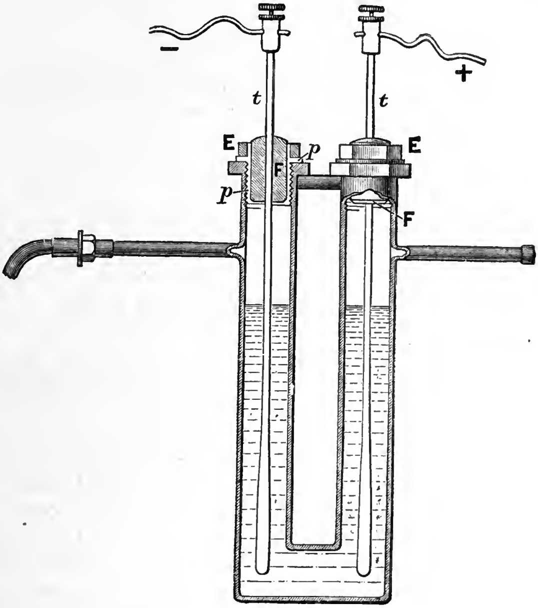


FIG. 211.—**U**-Tube in Moissan's Apparatus.

The apparatus is shown in Fig. 210. On the left is the **U**-tube, of 300 c.c. capacity, containing 60 gm. of acid potassium fluoride dissolved in 200 c.c. of anhydrous hydrofluoric acid. The electrodes are insulated by stoppers of fluorspar, covered outside with shellac (Fig. 211). The tube is immersed in a bath of methyl chloride, b.-pt. $-23°$, which is constantly renewed, and a potential of 50 volts applied. Hydrogen is evolved from the cathode; the fluorine coming from the anode, at the rate of about 5 litres per hour, is passed through a platinum or copper spiral, cooled in methyl chloride, and a tube of the same metal packed with fused sodium fluoride, to remove hydrofluoric acid. By collecting and measuring the hydrogen, and absorbing the fluorine in iron wire in a weighed tube, Moissan found that for every gram of hydrogen evolved from the cathode the iron increased in weight by 19 grams. The gas was therefore free fluorine. According to Moissan, the electrolyte is really potassium fluoride, the anhydrous hydrofluoric acid acting as an ionising solvent:

$$(-)\ H_2 + 2KF \leftarrow 2HF + 2K \overset{2KF}{\swarrow \quad \searrow} 2F \rightarrow F_2\ (+)$$

Fluorine has also been prepared by the electrolysis of fused KHF_2 or $NaHF_2$, in a copper vessel serving as the cathode; the anode was a graphite rod enclosed in a permeable diaphragm. Brauner (1894) also obtained small quantities of fluorine by heating potassium fluorplumbate, $PbF_4,3KF,HF$, procured by the action of hydrofluoric acid on potassium plumbate (p. 926). At 230–250° this loses hydrofluoric acid; at higher temperatures free fluorine is evolved:

$$PbF_4,3KF,HF = HF + PbF_4,3KF;$$
$$PbF_4,3KF = PbF_2,3KF + F_2.$$

Properties of fluorine.—Fluorine is a pale greenish-yellow gas, which, when once prepared, has very little action on glass below 100°, and may be kept in glass vessels. It has a powerful odour, resembling hypochlorous acid, but is not so poisonous as hydrofluoric acid vapour. By weighing the gas in a glass flask, Moissan found the density 19·21 ($H = 1$), from which the formula F_2 follows. The gas was liquefied in 1897 by Moissan and Dewar, who cooled it in liquid air boiling in a vacuum. It forms a clear yellow liquid, b.-pt. − 187°, sp. gr. 1·14. By cooling in liquid hydrogen, Dewar (1903) obtained solid fluorine, m.-pt. − 233°, also pale yellow in colour, but becoming colourless at − 252°.

Fluorine fumes in moist air, forming hydrofluoric acid and considerable amounts of ozone: $F_2 + H_2O = 2HF + O$. Fluorine is the **most active element known**; it forms no compounds with oxygen and chlorine, but combines with nearly every other element. It combines with bromine and iodine, forming BrF_3 and IF_5, both colourless liquids.

Fluorine unites with hydrogen explosively even at − 252°; sulphur, selenium, tellurium, phosphorus, iodine, bromine, arsenic, antimony, silicon, boron, carbon, and potassium all ignite spontaneously in the gas, and burn with the formation of fluorides. A jet of fluorine ignites at once in a jar of hydrogen, burning with a red-bordered flame, and producing HF, which attacks the glass jar. Lead and iron are rapidly attacked; magnesium, manganese, nickel, aluminium, and silver take fire when gently warmed. Gold and platinum are not attacked at the ordinary temperature, but are corroded and form fluorides on heating. Alcohol, ether, and turpentine take fire spontaneously in the gas. Potassium chloride is decomposed with evolution of chlorine:

$$2KCl + F_2 = 2KF + Cl_2.$$

By the action of fluorine on aqueous alkalies, hydrogen peroxide is formed. Fluorine can replace oxygen in many acids without producing much change in chemical properties, *e.g.*, it forms fluoriodates, $MF_2IO_2, IF_3(OH)_3$, and replaces oxygen in niobates and tantalates. The two elements are both strongly electronegative, and for this reason do not form compounds with each other. Since a mixture of fluorine and oxygen explodes when subjected to the silent discharge, it has been assumed that the element can combine with ozone.

Hydrofluoric acid, HF.—Hydrogen and fluorine combine with explosion under all conditions, forming **hydrogen fluoride,** or **hydrofluoric acid,** HF. This is more conveniently obtained by the action of acids on fluorides, or by heating acid potassium fluoride: $KHF_2 = KF + HF$.

If powdered fluorspar is distilled with concentrated sulphuric acid in a lead retort, connected with a lead receiver containing water (Fig. 212), the vapour of hydrofluoric acid dissolves in the latter to form a colourless, strongly-fuming liquid, which is a solution of hydrofluoric acid: $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. This attacks glass strongly, and is kept in lead or gutta-percha bottles. It is used for etching or engraving on glass. The latter consists of silicates of the metals of the alkalies and alkaline earths; the hydrofluoric acid removes the silica in the form of silicon fluoride: $SiO_2 + 4HF = SiF_4 + 2H_2O$. Etchings made with the liquid acid are clear; those made with the gas, or a mixture of aqueous acid and ammonium fluoride, are opaque.

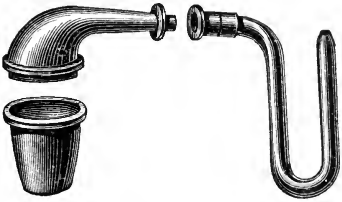


FIG. 212.—Lead Retort for preparation of Hydrofluoric Acid.

EXPT. 172.—A watch-glass is covered with beeswax by melting the latter on it and draining off the superfluous liquid. When the wax has hardened, a device is scratched through with a needle, and the glass placed over a lead dish containing a mixture of powdered fluorspar and concentrated sulphuric acid. The parts of the glass exposed will be found to be etched if the wax is removed after a few minutes by warming the glass.

The commercial acid contains about 40 per cent. of HF; its sp. gr. is 1·130. It is used for glass etching, for removing silica from canes, and as an antiseptic. The so-called "wild yeasts," which produce fusel oil in fermentation, are killed by small quantities of fluorides, whilst normal yeast-cells may be accustomed to the latter. Lactic and butyric fermentations are also inhibited. Sodium fluoride may be used for this purpose. Zinc and sodium fluorides are used in preserving wood.

If aqueous hydrofluoric acid is neutralised with caustic potash, and the liquid evaporated in a platinum dish, cubic crystals of **potassium fluoride,** KF, are obtained. If, to the neutralised liquid, a further equal volume of hydrofluoric acid is added and the liquid evaporated in a platinum dish, crystals of **potassium hydrogen fluoride,** KHF_2, or KF, HF, called **Fremy's salt,** are obtained. This may be dried by heating, and is relatively stable. If it is heated in a platinum retort, connected with a platinum condenser cooled by a freezing mixture, **anhydrous hydrofluoric acid** distils over (Fig. 213). The acid fluoride on heating forms the normal salt: $KHF_2 = KF + HF$. The anhydrous acid, first prepared in this way by Fremy in 1856, may also be obtained by heating lead fluoride in hydrogen: $PbF_2 + H_2 = Pb + 2HF$.

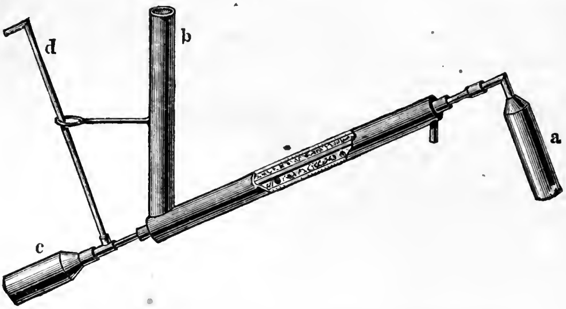


FIG. 213.—Platinum Retort and Condenser for preparing Anhydrous Hydrofluoric Acid.

Traces of moisture may be removed from hydrofluoric acid by electrolysis with platinum electrodes, when, as long as water is present, ozonised oxygen is evolved. When all the water is removed, the acid becomes non-conducting.

Anhydrous hydrofluoric acid is a colourless, strongly-fuming liquid, sp. gr. 0·988, boiling at 19·4°; it should therefore be kept in a freezing mixture. It does not solidify until cooled to $-102°$; the transparent, colourless solid melts at $-92·3°$. When quite free from water it does not attack glass or metals at the ordinary temperature, except potassium, which explodes in contact with the acid. In the presence of traces of water, the acid attacks glass violently, and dissolves most metals with evolution of hydrogen: $Fe + 2HF = FeF_2 + H_2$. The noble metals are not attacked, but gutta-percha (which resists the aqueous acid) and most organic materials are rapidly corroded. The acid and its vapour are dangerous corrosive poisons.

Aqueous hydrofluoric acid forms an acid of maximum boiling point, 120°, containing 36 per cent. of HF.

The **composition of hydrofluoric acid** was determined by Gore (1869), who heated silver fluoride at 100° in hydrogen in a platinum vessel, and obtained twice the volume of hydrofluoric acid gas. The formula at 100° is therefore HF: $2AgF + H_2 = 2HF + 2Ag$. Mallet (1881), by weighing the vapour at 30·5° in a glass flask coated inside with paraffin wax, obtained the density 19·66, corresponding with the formula H_2F_2. Thorpe and Hambly (1889) showed, by determining the vapour densities in a platinum flask at various temperatures and pressures, that the gas is associated, the density varying considerably with the temperature and pressure. At 88° and 741 mm. the molecular weight corresponds with HF; at lower temperatures it approximated to H_3F_3. No indication was found of the separate existence of H_2F_2, the density falling off continuously with rise of temperature, or diminution of pressure, to the limiting value corresponding with HF.

In concentrated solutions the acid appears, from freezing-point measurements, to be H_2F_2; in dilute solutions it has the formula HF.

The **fluorides** differ in many respects from the other halogen compounds. Silver fluoride is very soluble in water; calcium fluoride is nearly insoluble. The iron compound corresponding with cryolite, viz., $FeF_3, 3NaF$, is insoluble. If a standard solution of a ferric salt is added to a solution of sodium fluoride, this compound is precipitated, and if a little ammonium thiocyanate is added, the excess of ferric salt gives a red colour. Fluorides may be titrated in this way.

The fluorides also readily form complex and double salts with hydrofluoric acid: *e.g.*, HBF_4, H_2SiF_6, H_2NbOF_5, etc. The acid fluorides, such as KHF_2, may be regarded as derived from H_2F_2, which behaves as a dibasic acid.

The strength of hydrofluoric acid.—The heat of neutralisation of a strong acid by a strong base is always approximately the same, and equal to 13·7 kg. cal. (p. 295), this being the heat evolved in the reaction: $H^{\cdot}Aq. + OH'Aq. = H_2O$. Hydrofluoric acid, however, on neutralisation evolves 16·3 kg. cal., whilst if excess of the acid is added to the neutral salt, 0·3 kg. cal. is *absorbed*. Measurements of the conductivities of solutions of the acid show that it is much less ionised than the other halogen hydracids; in decinormal solutions the percentage ionisations of hydrofluoric and hydrochloric acids are 15 and 92, respectively. On neutralisation, the un-ionised molecules break up into ions as the reaction $H^{\cdot} + OH' = H_2O$ proceeds, and the abnormally large heat of neutralisation shows that heat is *evolved* in the reaction: $HF \rightleftharpoons H^{\cdot} + F'$. The absorption of heat on adding excess of acid is no doubt due to the formation of **acid salts**, *e.g.*, KHF_2.

The weak acetic acid has a nearly normal heat of neutralisation, 13·3 kg. cal.; hypochlorous acid has a very small heat of neutralisation, 9·8 kg. cal., since it is unable to neutralise an alkali in solution, on account of **hydrolysis**: $NaOCl \rightleftharpoons NaOH + HOCl$. Hydrochloric, hydrobromic, and hydriodic acids are about 92 per cent. ionised in decinormal solution; chloric and perchloric acids are almost as strong, whilst hypochlorous acid is only 0·02 per cent. ionised. Carbonic acid is 0·17 per cent. ionised, so that it is able to displace hypochlorous acid from its salts when the latter are exposed to air.

Atomic weight of fluorine.—Older determinations of the atomic weight of fluorine were based on the reaction $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. Since it is difficult to carry this to completion, somewhat varying results were found, the mean of good determinations being 18·85 (H = 1). By converting pure lime into calcium fluoride by treatment with hydrofluoric acid, the ratio $CaO : CaF_2 :: 1 : 1{\cdot}3932$ was found. Thus:

$$\frac{40 + 16}{40 + 2F} = \frac{1}{1{\cdot}3932}, \quad \therefore \quad F = 19{\cdot}01 \ (O = 16), \text{ or } 18{\cdot}9 \ (H = 1).$$

The halogens.—The elements fluorine, chlorine, bromine, and iodine are so obviously related in their chemical properties as to lead to their separation from the remaining elements to form a group, or family, which is called **the halogen group** (Greek *hals* = sea-salt). If we consider the properties of the free elements of the halogen group, and of their compounds, a marked **gradation** in the order given above is apparent. This is seen, in the first place, in the **physical properties of the elements**:—

Element.	Atomic weight.	Physical state.	Colour.	Melting point.	Boiling point.	Sp. gr. of liquid.	Solubility in water at 0°
Fluorine	18·9	gas	pale greenish-yellow	−233°	−187°	1·14	decomposes
Chlorine	35·18	gas	greenish-yellow (liquid yellow)	−102°	−33·6°	1·55	9·92 gm. per litre at 10°
Bromine	79·29	liquid	dark red (vapour red)	−7·3°	63°	3·19	41·5 gm. per litre
Iodine	125·91	solid	black (vapour violet)	113°	184·4°	5 (solid)	0·3 gm. per litre.

In a similar way, we may compare the **physical properties of the hydrogen compounds,** all of which are **acids :**

Compound	**Melting point.**	**Boiling point.**	**Density of liquid.**	**Heat of formation in kg. cal.**
HF (polymerised)	− 92·3°	19·4°	0·988/15°	—
HCl	−112·5°	−83°	0·929/0°	22
HBr	− 86°	−68·7°	1·78	12·1
HI	− 51·3°	−36·7°	—	− 6·1 (from *solid* iodine)

The physical properties of **hydrofluoric acid** are seen to be abnormal ; this results from the circumstance that it is **associated** even in the gaseous state below 80°, forming H_nF_n, whereas the other substances are normal. Polymerisation invariably leads to an increase of melting and boiling points. The abnormal ionisation of hydrofluoric acid has already been described.

The **stability of the hydrogen compounds,** as measured by their dissociation on heating, is in the order HF > HCl > HBr > HI, *i.e.*, in the order of the heats of formation. Thus, hydrogen iodide is appreciably dissociated at 360°, but hydrogen chloride only slightly at a white heat. The halogens also **displace** one another from their binary salts in the order of the heats of formation, viz. : F → Cl → Br → I. In the oxygen compounds, however, iodine displaces chlorine (p. 413) : $2KClO_3 + I_2 = 2KIO_3 + Cl_2$. The relation of the **stabilities of the oxygen compounds,** from fluorine (no oxide) to iodine (stable I_2O_5), to the heats of formation has already been considered (p. 391).

EXERCISES ON CHAPTER XXII

1. Describe the methods used for the preparation of bromine in the laboratory and in industry. What is the action of the element on (*a*) cold dilute caustic potash, (*b*) hot concentrated caustic potash, (*c*) mercuric oxide, (*d*) silver nitrate ?

2. How is bromic acid prepared ? What are its properties, and those of its salts ? How may a bromate be distinguished from a chlorate and an iodate ?

3. Describe the methods used in the manufacture of iodine. What impurities does the commercial substance contain, and how may they be separated ?

4. What is the action of heat on (*a*) bromine, (*b*) iodine, (*c*) hydriodic acid, (*d*) barium bromate, (*e*) barium iodate ?

5. How are the oxides of iodine prepared ? What formulæ are usually given to the oxy-compounds of iodine ?

6. Starting from iodine, how would you prepare (*a*) hydriodic acid, (*b*) iodic acid, (*c*) periodic acid ? Describe briefly the properties of

these substances, and compare them with the corresponding compounds of chlorine.

7. In what forms do bromine, iodine, and fluorine occur in Nature? How is hydrofluoric acid prepared from fluorspar?

8. How is anhydrous hydrofluoric acid prepared? By what means did Moissan prepare fluorine from this substance?

9. Describe the properties of fluorine, and explain why this element is included in the series of halogens.

CHAPTER XXIII

ATOMIC HEATS AND ISOMORPHISM

The determination of atomic weights.—The methods used in deciding which multiple of the **equivalent** of an element is the **atomic weight** have already been referred to briefly (p. 146). They include :

1. Determination of the least weight of the element found in the molecular weights of volatile compounds, the molecular weights being found from the vapour densities by **Avogadro's law** (p. 143) ; this requires that the element shall form *a number* of volatile compounds, which is not always the case.
2. The molecular weights of compounds may be determined in solution by the freezing-point, boiling-point, or vapour-pressure methods (Chapter XXI).
3. The **Atomic Heat** method, applicable to solid elements, especially metals.
4. **Isomorphism.**
5. **Chemical analogies** with compounds of elements of known atomic weight.
6. The **ratio of the specific heats of gases** (pp. 146, 598).
7. The **Periodic Law** (Chapter XXIV).

The application of as many of these methods as possible gives a valuable check on the atomic weight. Thus, if the atomic weight has been fixed approximately from the specific heat, the vapour density of *one* volatile compound may be most valuable in confirmation, although alone it could not have given certain results, since then it could not be assumed that the compound contained only one atom of the element.

Atomic heats, and isomorphism, will be considered in the present chapter ; the Periodic Law is discussed in the following chapter.

ATOMIC HEATS.

Dulong and Petit's Law.—P. L. Dulong and A. T. Petit, in 1819, discovered a very simple relation between the **atomic weights** and **specific heats** of **solid elements,** viz., that the product of the two, which they called the **atomic heat,** is constant. **Dulong and Petit's law** asserts that **the atomic heats of solid elements are constant, and approximately equal to 6·3.**

Quantities of solid elements in the proportion of their atomic weights are therefore raised through 1° in temperature by identical quantities of heat. The heat capacity of a solid element is a property of its atoms: Dulong and Petit expressed their result in the statement: *the atoms of all solid elements have the same capacity for heat.* By assuming that half the energy of a monatomic solid, due to atomic vibration, is kinetic, and half potential (as in the vibrations of a pendulum), and that the kinetic energies of the atom of the solid and that of a monatomic gas are equal at the same temperature, Boltzmann (1871) arrived at the result that the atomic heat of the solid is double that of the monatomic gas, viz., $2 \times 3 = 6$ cal. (p. 598). The following table gives the results determined near atmospheric temperature.

TABLE OF ATOMIC HEATS.

Element.	**Atomic weight** (H = 1)	**Specific heat** (20° to 100°)	**Atomic heat = Atomic weight × Specific heat.**
Arsenic	74·5	0·0827	6·16
Bismuth	206·5	0·0303	6·27
Bromine (solid) ...	79·3	0·084	6·65
Calcium	40	0·17	6·80
Cobalt	58·5	0·1030	6·05
Copper	63	0·0936	5·90
Gold	196	0·0316	6·20
Iodine	126	0·054	6·80
Iron	55·5	0·1146	6·35
Lead	206	0·0314	6·52
Lithium	6·9	0·94	6·48
Magnesium ...	24	0·2492	5·95
Mercury (solid) ...	199	0·0335	6·66
Nickel	58	0·1092	6·32
Phosphorus (yellow)	31	0·1981	6·15
Platinum	194	0·0320	6·20
Silver	107	0·0566	6·06
Sulphur	32	0·1780	5·70
Tin	118	0·0556	6·55
Uranium	236	0·0276	6·50
Zinc	65	0·0931	6·05
		Mean atomic heat =	6·30

In order to obtain agreement with the law, Dulong and Petit found it necessary to alter some of the atomic weights current at the time: with one or two exceptions these modifications have been confirmed.

The **exceptions to Dulong and Petit's law,** which all give atomic heats lower than 6·3, occur among elements of *low atomic weight and high melting point.* Thus, although lithium (at. wt. 7; m.-pt. 180°) and sodium (at. wt. 23; m.-pt. 97·6°) conform to the law, the following elements, with atomic weights lower than 30, all have atomic heats considerably below 6·3:

Element.	**Melting point.**	**Atomic weight.**	**Specific heat at 15°**	**Atomic heat at 15°**
Beryllium ...	1300°	9	0·3756	3·4
Boron (cryst.)	above 2000°	11	0·239	2·64
Carbon (diamond)	do.	12	0·113	1·35
,, (graphite)	do.	12	0·160	1·92
Silicon (cryst.)	*c.* 1200°	28	0·170	4·75

Weber (1875), however, found that the specific heats of boron, carbon, and silicon increase fairly rapidly with the temperature at which the determination is carried out, and the same result was found for beryllium by Humpidge (1885).

Diamond.		**Graphite.**		**Boron.**		**Silicon.**		**Beryllium.**	
°C.	At ht.	°C.	At ht.	°C.	At. ht.	°C.	At. ht.	°C.	At. ht.
− 50	0·76	− 50	1·37	− 40	2·11	− 40	3·81	0	3·42
10·7	1·35	10·8	1·92	26·6	2·62	21·6	4·75	100	4·28
58·3	1·84	61·3	2·39	76·7	3·01	86	5·32	200	4·93
140	2·66	201·6	3·56	177·2	3·63	184·3	5·63	300	5·38
247	3·63	249·3	3·90	233·2	4·33	232·4	5·68	400	5·61
615	5·33	640	5·40	—		—		500	5·65
808	5·44	832	5·42	—		—		—	
980	5·47	980	5·63	—		—		—	

At high temperatures, the atomic heats of these elements approach the normal value, 6·3. The variation with temperature is shown by the curves of Fig. 214. The atomic heats of other elements, which have the normal value 6·3 at the ordinary temperature, also increase somewhat with the temperature, but not to the same extent as those with abnormal atomic heats.

Thus, the atomic heats of platinum at 18–100°, and 1230°, are 6·2 and 8·84, respectively.

Atomic heats at low temperatures.—The fact that the atomic heats of boron, carbon, silicon, and beryllium become larger, and approach the normal values, as the temperature rises, suggests that the elements with normal atomic heats may be, at the ordinary temperature, in a region which is only attained at higher temperatures by the former elements. In this case the atomic heats of the elements which behave normally should become abnormally small at low temperatures. This has been found by experiment to be the case. The atomic heats of all solid elements fall to small values at low temperatures, some more rapidly than others, and it is probable that at the absolute zero, — 273°, the atomic heats are all zero. In the case of the diamond, the atomic heat is actually zero at temperatures below — 230°.

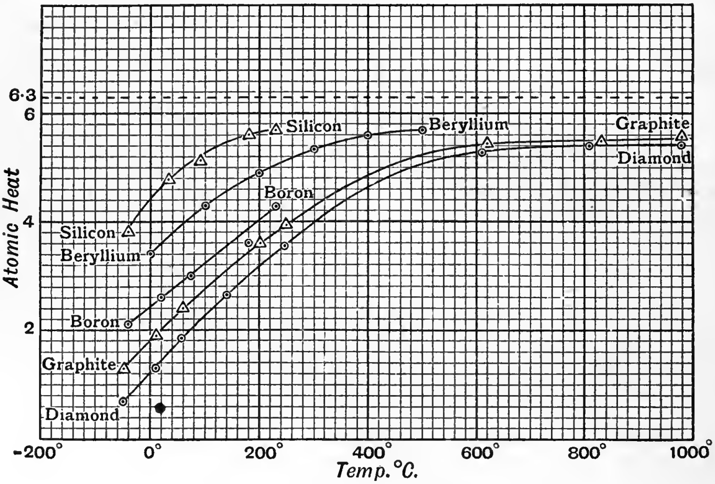


FIG. 214.—Atomic Heat Curves.

Element.		Atomic heat +20° to 100°	Atomic heat — 188° to + 20°	Atomic heat —253° to —195°
Carbon	...	2·4	1·15	0·03
Aluminium	...	5·9	4·73	1·12
Silicon	...	5·2	3·34	0·77
Iron ...	...	6·4	4·80	0·98
Copper	...	6·2	4·88	1·22
Zinc ...	...	6·1	5·53	2·52
Silver ...	...	6·1	5·51	2·62
Lead ...	...	6·4	6·21	4·96

The values for the diamond at low temperatures are :

Temperature °C....	896	85	— 41	— 64	— 181	— 231	— 243
Atomic heat ...	5·45	2·12	0·86	0·66	0·03	0·00	0·00

The dependence of atomic heat on temperature is shown for a few elements in the curves of Fig. 215, from the experiments of Nernst.

The following results were obtained by Kamerlingh Onnes and Keesom (1915), at the temperatures of liquid hydrogen :

Lead.		Copper.	
Temp. abs.	Atomic heat.	Temp. abs.	Atomic heat.
14·19°	1·56	15·24°	0·05
22·31°	2·98	21·505°	0·14
46·25°	5·04		

The quantum theory.—The rapid diminution of the specific heats of solids at low temperatures, and the convergence to zero in the neighbourhood of the absolute zero, is in agreement with the **theory of energy quanta,** due to Planck (1906). According to this theory, the atoms of a solid do not take up heat energy continuously, but in finite amounts, called **quanta,** which may be considered as atoms of energy. The value of the quantum, ϵ, varies from element to element, and is equal to $h\nu$, where h is a universal constant, equal to $6{\cdot}55 \times 10^{-27}$, known as **Planck's constant,** and ν is the **atomic frequency,** characteristic of each element. In the case of sodium, for instance $h\nu = \epsilon = (6{\cdot}55 \times 10^{-27}) \times (5{\cdot}01 \times 10^{14}) = 3{\cdot}28 \times 10^{-12}$ ergs, which is about one-sixtieth the kinetic energy of a hydrogen molecule at 0°. This value of ν is the frequency of the light emitted by incandescent sodium vapour.

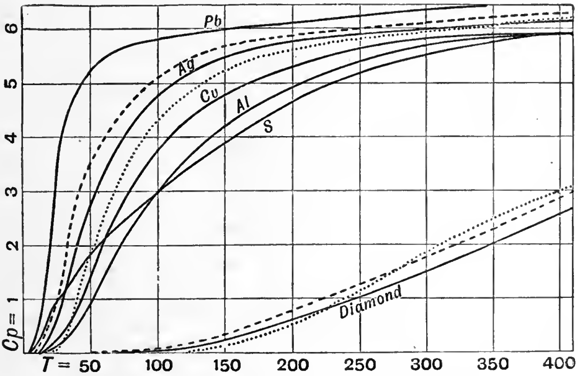


FIG. 215.—Atomic Heats at Low Temperatures.

The "deviations" from Dulong and Petit's law at low temperatures are explained by the theory of energy quanta ; the former law is a limiting case of a more general law deducible from the new theory. According to this, the atomic heat of a monatomic solid element is given by the expression, due to Einstein (1907) :

$$\text{Atomic heat} = 3R\,\frac{x^2\,e^x}{(e^x - 1)^2}\,;$$

where $x = \beta\nu/T$, the constant β being equal to Planck's constant

h divided by the gas constant, R, in absolute units (p. 149) and multiplied by Avogadro's constant, **N** (p. 268):

$$\beta = \frac{h\mathbf{N}}{R} = \frac{(6{\cdot}55 \times 10^{-27}) \times (6 \times 10^{23})}{8{\cdot}3 \times 10^{7}} = 4{\cdot}8 \times 10^{-11}.$$

Planck's theory leads to the assumption of the **atomic structure of radiation:** this is also made up of quanta, $h\nu$, where ν is the frequency. The "critical energy" of a molecule (p. 354) also appears to be of the form $h\nu$, where ν is the frequency of some type of radiation absorbed by the substance.

According to Debije, the atomic heats at very low temperatures should be proportional to the cube of the absolute temperature: At. ht. $= kT^3$. This has been confirmed by Nernst and others.

Atomic weights from specific heats.—Dulong and Petit's law obviously gives an approximate value of the atomic weight of a solid element if the specific heat is known:

$$\text{Atomic weight} = 6{\cdot}3 \div \text{Specific heat.}$$

Thus, an analysis of a volatile **chloride of uranium** shows that it has the following percentage composition:

Uranium	62·66
Chlorine	37·34
	100·00

The **equivalent** of uranium, or the weight combining with 35·2 parts of chlorine, is $62{\cdot}66 \times \frac{35{\cdot}2}{37{\cdot}34} =$ **59·1.** The **vapour density** of the chloride was found by Zimmermann to be 193 (H = 1), hence the *approximate* **molecular weight** is 191 × 2 = 382. This will contain $37{\cdot}34 \times \frac{382}{100} = 142{\cdot}5$ parts, which is nearly equal to 4 × 35·2 = 140·8 parts, or four atoms, of chlorine. The **formula** of the chloride is therefore U_xCl_4, where $x = 1, 2, 3, 4 \ldots$ etc.

The weight of uranium in a molecular weight of the chloride is, *approximately*, 382 – 142·5 = 239·5. But this is very nearly equal to 4 × 59·1 = 236·4, *i.e.*, four times the *accurately* determined equivalent. Thus, $U_x = 236{\cdot}4$. It has still to be decided whether this is the atomic weight of uranium, or a multiple of it. Thus, the following formulæ of the chloride are possible:

Formula.	**At. wt. of Uranium.**
UCl_4	236·4
U_2Cl_4	118·2
U_3Cl_4	78·8
U_4Cl_4	59·1

To decide which of these is the correct formula, an *approximate* value of the atomic weight of uranium must be found. The **specific heat** of solid metallic uranium is 0·0276; hence, by Dulong and Petit's law, the **atomic weight** is *approximately* $6{\cdot}3/0{\cdot}0276 = 228$. This shows that the *exact* value is 236·4, and hence the formula of the chloride is UCl_4.

It must be carefully noticed that the value of the atomic weight deduced from Dulong and Petit's law is *approximate* only, and is used to decide on a particular multiple of the *exact* equivalent. The molecular weight of the compound is also found from the exact chemical analysis.

The more exact expressions for the atomic heat derived from the quantum theory lead to more accurate values of the atomic weights, but not so accurate as those found by exact chemical analysis.

Molecular heat of a compound.—An extension of Dulong and Petit's law to **solid compounds** was made by F. Neumann in 1831. He found that **the specific heats of solid substances of similar composition are inversely proportional to their molecular weights.** Thus:

Substance.	Molecular weight.	Specific heat.	Molecular heat.
Calcium carbonate, $CaCO_3$ ...	100	0·2044	20·44
Magnesium carbonate, $MgCO_3$	84	0·2270	19·1
Ferrous carbonate, $FeCO_3$ ...	116	0·1819	21·1
Zinc carbonate, $ZnCO_3$ ...	125	0·1712	21·4
Barium carbonate, $BaCO_3$ ...	196	0·108	21·1
Lead carbonate, $PbCO_3$ ...	266	0·081	21·6

The **molecular heat** of a solid compound is the product of its specific heat and its molecular weight. Neumann's law shows that the molecular heats of *similar* compounds are alike. The molecular heats of the carbonates of the alkaline-earth metals, etc., of the general formula RCO_3, are 20 (approximately); the sulphates, RSO_4, of the same metals have a molecular heat of about 25.

The relation between Neumann's law and that of Dulong and Petit was pointed out by Joule in 1844. **Joule's law** (often called **Woestyn's law**) states that **the molecular heat of a solid compound is the sum of the atomic heats of its constituents.**

This was confirmed by the experiments of Kopp (1865). It indicates that the atomic heat of an element is unchanged by combination, or the molecular heat of a solid compound is additively composed of the atomic heats of its elements. The heat content of any solid, therefore, seems to reside in its *atoms*. With gases, the case is quite different (p. 598), since the kinetic energy of the *molecule* is predominant.

An example of Joule's law is the calculation of the molecular heat of silver iodide :

Atomic heat of silver = 107 × 0·057 = 6·10
Atomic heat of iodine = 126 × 0·054 = 6·80

Sum of atomic heats = 6·1 + 6·8 = 12·9
Molecular heat of silver iodide = molecular weight × specific heat = 233 × 0·061 = 14·2

The molecular heats of lead bromide and iodide may also be calculated from the sums of the atomic heat of lead and twice the atomic heat of the halogen :

$PbBr_2$ = 6·48 + 2 × 6·65 = 19·78
$Pb\ I_2$ = 6·48 + 2 × 6·80 = 20·08
(Pb + 2 Br) × sp. ht. of lead bromide = (206 + 2 × 79·3) × 0·0533 = 19·4
(Pb + 2I) × sp. ht. of lead iodide = (206 + 2 × 126) × 0·0427 = 19·6

The agreement, as will be seen, is only approximate.

It is possible to calculate by means of Joule's law the atomic heats of elements in the solid state in cases where these cannot be directly determined. Thus, the atomic heat of solid chlorine may be calculated as follows :

Specific heat of silver chloride = 0·091 ∴ molecular heat of AgCl = 0·091 × (107 + 35·2) = 12·96. This, however, is the sum of the atomic heats of silver and of *solid* chlorine ; hence :
atomic heat of solid chlorine = molecular heat of silver chloride — atomic heat of silver = 12·96 — 6·10 = 6·86.

From the molecular heats of their compounds, Kopp deduced the following atomic heats :

Boron	2·7	Phosphorus	5·4
Carbon	1·8	Sulphur	5·4
Silicon	4	—	

These agree quite well with the values determined directly at 0°–100°, although they are all abnormal. The abnormal atomic heats are therefore preserved in combination. The calculated values for solid oxygen, nitrogen, and fluorine are also abnormal, as would be expected since these elements are non-metals of low atomic weights.

Molecular heat of calcium carbonate $= (39{\cdot}8 + 11{\cdot}9 + 3 \times 15{\cdot}88) \times 0{\cdot}206 = 20{\cdot}4$. Sum of atomic heats of calcium and carbon $= 6{\cdot}8 + 1{\cdot}8 = 8{\cdot}6$ $\therefore$ atomic heat of solid oxygen $= \frac{1}{3}(20{\cdot}4 - 8{\cdot}6) = 3{\cdot}9$.

Molecular heat of ice $= 18 \times 0{\cdot}92 = 16{\cdot}5$; atomic heat of solid oxygen $= 3{\cdot}9$ $\therefore$ atomic heat of solid hydrogen $= \frac{1}{2}(16{\cdot}5 - 3{\cdot}9) = 6{\cdot}3$, which is the normal value.

The extension of the quantum theory to compounds is still incomplete. Nernst suggests that the energy of the molecules themselves can be calculated from Debije's T^3 formula, whilst that of the atoms in them follows Einstein's law.

CRYSTALLOGRAPHY

Crystals.—A distinction has already been drawn between **crystalline** and **amorphous** substances. The most obvious difference between the two is that of **external form**: whereas amorphous solids are found in irregularly-shaped pieces, **crystals** usually have definite shapes, by which they are recognised. Another difference is in the **fracture**: crystals break into more or less similarly-shaped pieces, with plane faces meeting in sharp edges, whilst amorphous solids, such as glass or pitch, break into very irregular pieces, showing curved faces, with concentric rings, such as are seen inside an oyster-shell. These two kinds of fracture are known as **crystalline fracture** and **conchoidal fracture,** respectively.

A crystalline substance may, however, be recognised even if in powder, and with no apparent external form. With the exception of crystals of the regular system (see below), all fragments of crystals act upon polarised light, and if the powder is examined under a microscope so arranged that the light passes through a pair of crossed Nicol prisms, and is therefore totally extinguished, it is found that light passes through the crystal grains, which are seen beautifully coloured on a dark ground. Again, if a crystal of gypsum is touched with a red-hot needle on one of its faces, a white patch of anhydrous calcium sulphate develops (Fig. 216): $CaSO_4{,}2H_2O = CaSO_4 + 2H_2O$. This patch is not circular, but elliptical, showing that the heat is conducted through the crystal more readily in one direction than in the perpendicular direction.

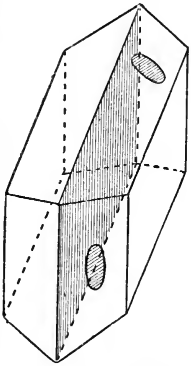


FIG. 216.—Crystal of Gypsum showing Plane of Symmetry.

We thus are able to recognise some definite internal arrangement, or **internal structure,** in the crystal, and the outer form is determined by this structure. Even if the outer form is destroyed by breaking, or grinding, the internal structure corresponding with it remains, and may be recognised. If, however, the above experiments are tried with a piece of glass, which is an amorphous solid, it is found that no light passes under crossed Nicols, and if the glass is coated with paraffin wax, the latter is melted in a circular patch when a hot needle is pressed upon the solid. The results are the same even if the glass has been cut into any external form like that of a crystal: the resemblance to a crystal is spurious, and the glass remains all the time an amorphous body. The internal structure is more important than the external form.

The definite internal structure of crystals is almost certainly due to some definite or ordered arrangement of the atoms or molecules in the crystal: this arrangement can be detected by the reflection of X-rays from the crystal faces (p. 1018). The molecular structure is found to be **symmetrical,** *i.e.*, a definite pattern will be repeated over and over again in definite directions in space, in the same way, for instance, as the pattern of a wall-paper. To the **internal symmetry** of the arrangement of the atoms or molecules there also corresponds an **external symmetry** of the **crystal form.**

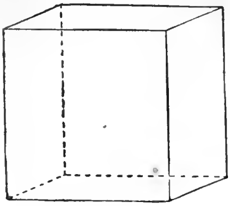


FIG. 217.—Cube.

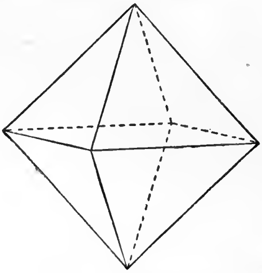


FIG. 218.—Octahedron.

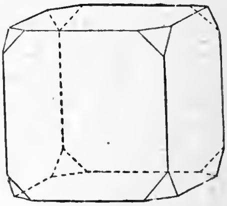


FIG. 219.—Combination of Cube and Octahedron.

Symmetry of crystals.—The symmetry of a crystal form is determined by regularities in the positions of the similar faces, edges, etc., of the crystal. A crystal having all its faces alike is termed a **simple form.** Thus, both the **cube** in Fig. 217 and the **octahedron** in Fig. 218 are simple forms, because all the faces of the first are identical squares, and all those of the second are identical equilateral triangles. A crystal having sets of faces corresponding with two or more simple forms is called a **combination form.** Thus, the crystal of galena (PbS) shown in Fig. 219 is a combination of the cube and the octahedron, since it contains sets of faces derived from each.

The regularities in the positions of faces, edges, etc., *i.e.*, the **symmetry** of the crystal, are defined in terms of **planes of symmetry, axes of symmetry,** and a **centre of symmetry.** A **plane of symmetry** divides a crystal into two similar and similarly-placed halves, each being the mirror-image of the other. Thus, a crystal of gypsum is divided by the plane shown in Fig. 216 into two similar and similarly-placed halves; this is the only plane of symmetry possessed by the gypsum crystal. An **axis of symmetry** is defined as an axis such that, if the crystal is rotated around it, the crystal occupies the same position in space more than once in a complete turn. Thus, the axis shown in Fig. 220 is an axis of fourfold symmetry, since the cube takes up the same position in space four times on rotation through 360° about this axis. Axes of two-, three-, four-, and six-fold symmetry occur, when the crystal comes to occupy the same position in space 2, 3, 4, or 6 times in a complete revolution, *i.e.*, on rotation through 180°, 120°, 90°, or 60°.

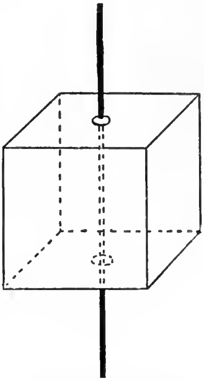


FIG. 220.—Axis of Symmetry of Cube.

A crystal has a **centre of symmetry** when like faces are arranged in pairs in corresponding positions on opposite sides of a central point.

An examination of a cube shows that it possesses 9 planes of symmetry (Fig. 221); it has 13 axes of symmetry (3 of fourfold, 4 of threefold, and 6 of twofold symmetry), and a centre of symmetry. It is therefore said to possess 23 **elements of symmetry,** which is the highest number possible in a crystal. Some crystals have no plane of symmetry, others have no axes of symmetry, others have no centre of symmetry, and a few have no element of symmetry at all.

The **crystallographic symmetry** depends on the internal molecular structure, and need not correspond with the **geometrical symmetry** except in the perfect crystal, since the crystal may have certain faces developed to a greater extent than others. The **angles between the faces,** however, are the same both in the ideal crystal and in the actual, distorted, crystals, and these angles are the important measurements in determining the crystal form. Thus, the angles between the faces of the perfect and distorted octahedra in Fig. 222 are identical.

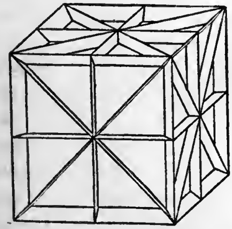


FIG. 221.—Planes of Symmetry of Cube.

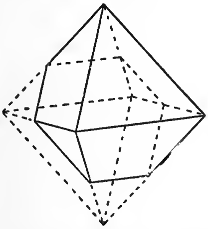


FIG. 222.—Ideal and Distorted Octahedra, showing Constancy of Angles between the Faces.

Crystallographic systems.—It has been shown mathematically that thirty-two types of symmetry, differing in the degree and nature of the elements of symmetry, are possible among crystals, so that the latter may be classified into **symmetry groups.** Of these, eleven only include practically all the common substances.

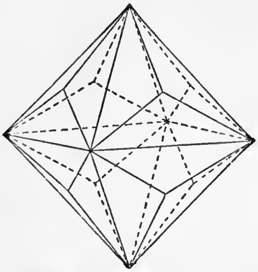


FIG. 223.—Triakisoctahedron (Three-faced Octahedron).

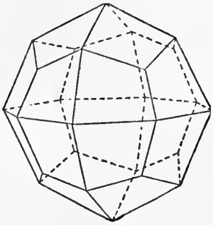


FIG. 224.—Icositetrahedron.

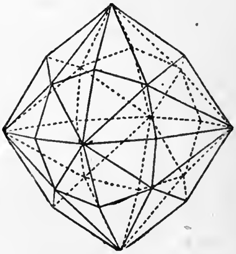


FIG. 225.—Hexakisoctahedron (Six-faced Octahedron).

The usual method of classification, however, is into what are known as **crystal systems.** These are related to the **crystallographic axes.** The position of any **crystal face** is defined by the intercepts made on three axes intersecting in a point inside the crystal. If a suitable number of axes of symmetry exists, three of them may be chosen as crystallographic axes, but the latter need not be the axes of symmetry.

The following types of crystallographic axes occur :

1. *Three equal axes at right angles :* this corresponds with the **cubic,** or **regular**, system.

Fig. 218 shows the **regular octahedron**, which is the typical **pyramid form** of the regular system. Fig. 217 is the **cube,** which is the typical **prism form** of the system. The other simple forms (*cf.* above) of the regular system are the **triakisoctahedron** (Fig. 223), the **icositetrahedron** (Fig. 224), the **hexakisoctahedron** (Fig. 225), the **rhombdodecahedron** (Fig. 226), and the **tetrakis-hexahedron** (Fig. 227). Combinations of these forms also occur.

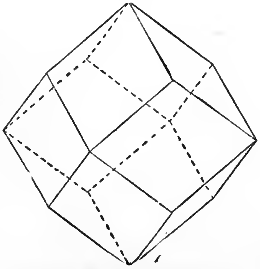


FIG. 226.—Rhombdodecahedron.

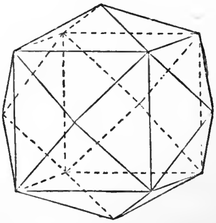


FIG. 227.—Tetrakis-hexahedron (Four-faced Cube).

Examples of substances occurring in the regular system are :
octahedron : alums, magnetite (Fe_3O_4), cuprite (Cu_2O) ;
cube : fluorspar, common salt, sylvenite (KCl) ;
rhombdodecahedron : garnet ;
tetrakis-hexahedron, etc., iron pyrites (FeS_2).

(2) *Two equal axes meeting at right angles, and a third, longer or shorter, axis meeting these at right angles.* This constitutes the **tetragonal system.** Typical pyramid and prism forms are shown in Figs. 228—231. There are two orders of pyramid and prism forms, according as the horizontal axes terminate at the angles (Figs. 228 and 230), or the middle point (Figs. 229, 231), of the faces.

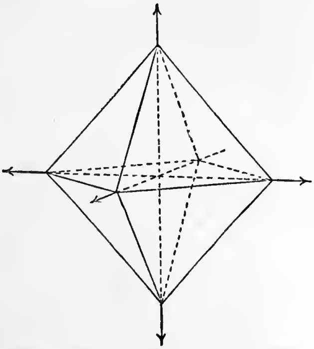


FIG. 228.—Tetragonal Bipyramid : First Order.

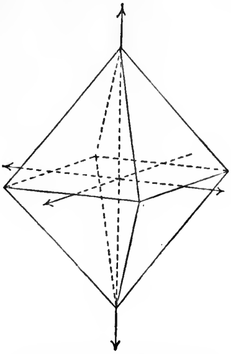


FIG. 229.—Tetragonal Bipyramid : Second Order.

Zircon (Zr_2SiO_4), potassium dihydrogen phosphate (KH_2PO_4), and tinstone (SnO_2) show prism and pyramid forms ; potassium ferrocyanide gives chiefly pyramid forms.

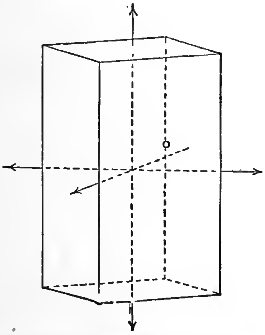


FIG. 230.—Tetragonal Prism : First Order.

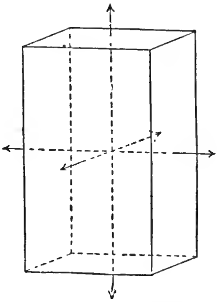


FIG. 231.—Tetragonal Prism : Second Order.

If the length of the vertical axis (*AB*) in this (and other) systems be denoted by *c*, and the length of the horizontal axes by *a* and *b*, with appropriate signs, as shown in Fig. 232, the cubic system may be denoted by (*a a a*), and the tetragonal system by (*a a c*).

(3) In the **hexagonal system** there are *four axes, three equal and intersecting in the same plane at angles of 60°, and a fourth axis, greater or less than these, at right angles* (*a a a c*). Here again there are two types of pyramid and prism forms, according as the lateral axes meet angles or the mid-points of faces.

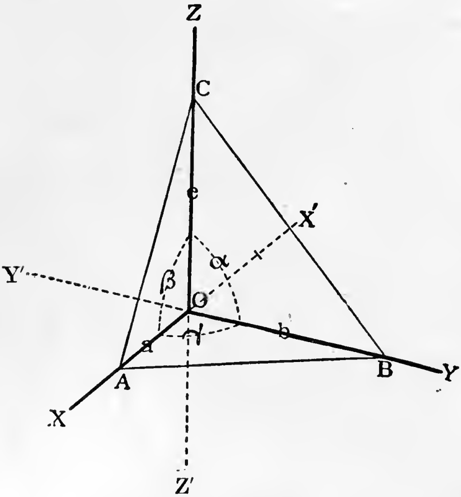


FIG. 232.—Crystallographic Axes.

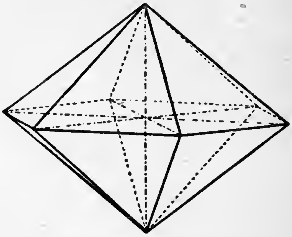


FIG. 233.—Hexagonal Bipyramid: First Order.

Typical pyramid forms are shown in Figs. 233 and 234; prism forms are shown in Figs. 235 and 236. Examples of this form are witherite ($BaCO_3$), beryl, and apatite.

(4) In the **rhombic system** there are *three unequal axes all at right angles* (*a b c*). Any one of these may be taken as the **vertical axis** (*c*), the other two being then **lateral axes.** The longer lateral axis is called the **macro-axis,** the shorter is the **brachy-axis.**

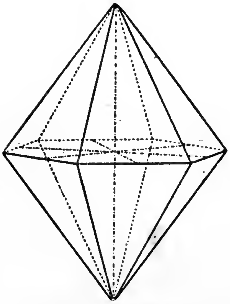


FIG. 234.—Hexagonal Bipyramid: Second Order.

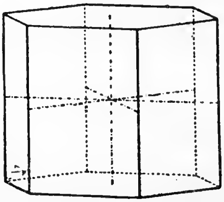


FIG. 235.—Hexagonal Prism: First Order.

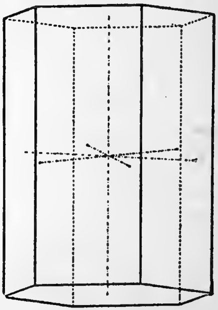


FIG. 236.—Hexagonal Prism: Second Order.

Pyramid (Fig. 237) and prism (Fig. 238) forms exist, but new types of faces, known as **domes** and **pinakoids,** are met with in the rhombic system. Prism faces developed parallel to one of the lateral axes, and intersecting the other two axes, are called **dome faces.** If they are parallel to the longer, or macro-axis, these are called **macrodomes** (Fig. 239); if parallel to the shorter, or brachyaxis, they are called **brachydomes** (Fig. 240).

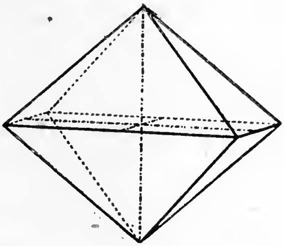


FIG. 237.—Rectangular Rhombic Bipyramid.

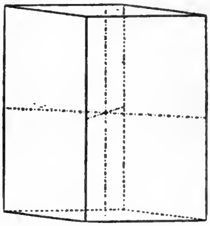


FIG. 238.—Rhombic Prism.

Prism faces intersecting one lateral axis and parallel to the other two axes are called **pinakoid faces; macropinakoids** intersect the macro-axis; **brachypinakoids** the brachy-axis. These are the diamond-shaped end faces in Figs. 239 and 240. In Fig. 241, representing a crystal of barytes ($BaSO_4$), the faces marked 010 constitute a macropinakoid form, or in this case a **basal pinakoid;** the faces 101 are the macrodome form. The faces belonging to the prism form are marked 001.

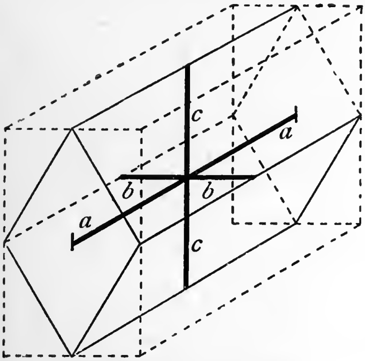


FIG. 239.—Dome and Pinakoid Faces: Macrodome.

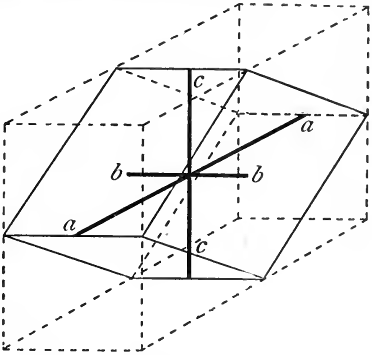


FIG. 240.—Dome and Pinakoid Faces: Brachydome.

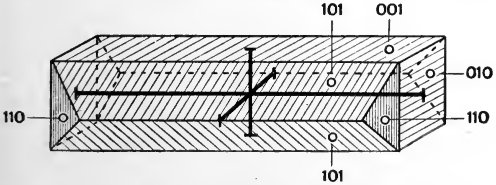


FIG. 241.—Barytes Crystal.

Sulphur occurs in pyramid forms of the rhombic system; pyramid and prism forms are shown by zinc sulphate, and stibnite (Sb_2S_3); dome forms occur in aragonite ($CaCO_3$), barytes, and potassium sulphate; pinakoid forms occur on crystals of anhydride ($CaSO_4$).

(5) In the **monoclinic system** there are *three axes, all of different lengths; two of the axes intersect one another at an oblique angle, whilst the third is at right angles to the plane of the other two.* Pyramid and prism forms, pinakoids, and domes occur. The vertical axis is denoted by c; the b-axis, or **ortho-axis,** is at right angles to the vertical axis, whilst the inclined, or a-axis, is the **clino-axis**. The angle between the vertical axis and clino-axis is called the **angle β.**

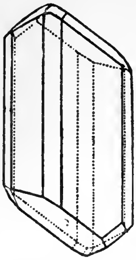


FIG. 242.
Triclinic Crystal (Copper Sulphate, $CuSO_4,5H_2O$).

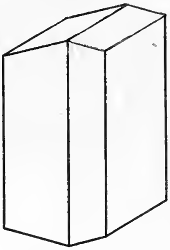


FIG. 243.—Triclinic Crystal (Potassium Dichromate).

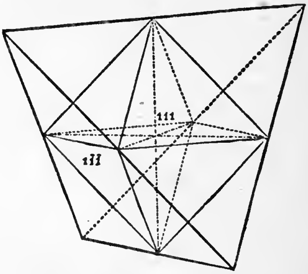


FIG. 244.—Relation of Tetrahedron (Hemihedral Form) to Octahedron (Holohedral Form).

An example of a monoclinic crystal is gypsum (Fig. 216); green vitriol, washing-soda, borax, cane-sugar, and oxalic acid crystallise in this system.

(6) In the **triclinic system** there are *three unequal axes intersecting one another obliquely.* One of these is selected as the vertical axis, the other two are then spoken of as the macro-axis (longer), and the brachy-axis (shorter). The three angles between the axes are also given (α, β, γ). Examples of crystals belonging to this system are copper sulphate (Fig. 242), potassium dichromate (Fig. 243), and soda-felspar.

Hemihedral forms.—Those forms in any system which exhibit the full number of faces required by the symmetry of the system are called **holohedral forms.** If only half the number of faces occurring in the holohedral form are present, the form is known as **hemihedral.** Forms exhibiting only one quarter the full number of faces required by the symmetry of the system are called **tetartohedral.** (In modern classification into symmetry groups, these forms go as holohedral forms into separate classes.)

Thus, a hemihedral form is produced by suppressing half the faces of the holohedral form, and producing the remainder so as to meet in new edges. Fig. 244 shows the form obtained by producing alternate faces of the regular octahedron : this is the **regular tetrahedron**, having four faces instead of eight. The tetrahedron is the hemihedral form of the octahedron.

Important hemihedral forms occur in the **hexagonal system.** By developing alternate faces of the hexagonal pyramid (Fig. 245), one obtains the positive or negative **rhombohedron** (Figs. 246, 247). From the dihexagonal pyramid, with 24 faces, obtained by the combination of two hexagonal pyramids, two kinds of hemihedral forms are produced: (i) by suppressing alternate pairs of faces (Fig. 248) one obtains the **scalenohedron** (Fig. 249) ; (ii) by suppressing alternate faces (Fig. 250) the **trapezohedron** (Fig. 251) results. Calcite ($CaCO_3$) occurs as scalenohedra and rhombohedra ; quartz occurs in trapezohedra : hæmatite (Fe_2O_3), calamine ($ZnCO_3$,), potassium and sodium nitrates, magnesite ($MgCO_3$), witherite ($BaCO_3$), and strontianite ($SrCO_3$) occur as rhombohedra.

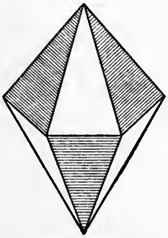


FIG. 245.—Hexagonal Pyramid : Shaded Faces to be Suppressed.

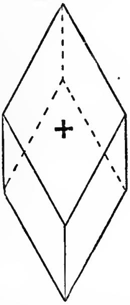


FIG. 246.—Hemihedral Form of Hexagonal Pyramid : Positive Rhombohedron.

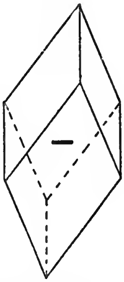


FIG. 247.—Hemihedral Form of Hexagonal Pyramid : Negative Rhombohedron.

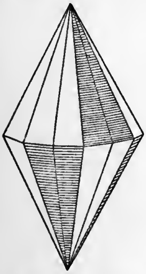


FIG. 248.—Dihexagonal Pyramid : Alternate Pairs of Faces to be Suppressed.

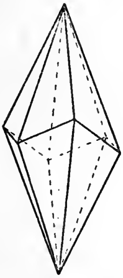


FIG. 249.—Scalenohedron: Hemihedral Form obtained from Fig. 248.

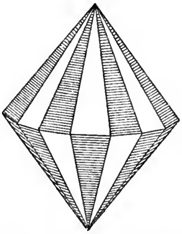


FIG. 250.—Dihexagonal Pyramid : Alternate Faces to be Suppressed.

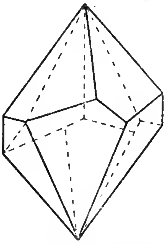


FIG. 251. — Trapezohedron : Hemihedral Form obtained from Fig. 250.

Twin crystals.—Two or more individual crystals sometimes grow in contact so that neither is complete, and **twin crystals** (Figs. 252 and 253) are formed. The two crystals may coalesce except for a few faces, as in Fig. 254.

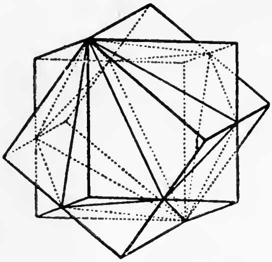


FIG. 252.—Twin Crystal of Fluorspar.

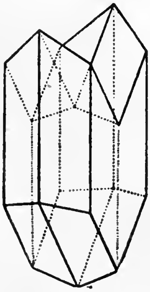


FIG. 253.—Twin Crystal of Gypsum.

Further particulars of crystallographic notation, etc., must be obtained from the regular text-books, *e.g.*, Tutton's "Crystallography" (Macmillan).

In the study of crystallography, however, the use of models, and the examination of actual crystals, must accompany the reading.

ISOMORPHISM

Isomorphism.—Haüy (1743–1822), the founder of the science of crystallography, laid down as fundamental axioms that: (i) identity of crystalline form (except in the cubic system) implies identity of chemical composition; and, conversely, (ii) difference in crystalline form implies difference in chemical composition.

Exceptions to these statements were, however, known at the end of the eighteenth century. Klaproth (1788) showed that calcium carbonate crystallised in the hexagonal form as calcite, and in the rhombic form as aragonite. Romé de l'Isle (1772) observed that, from mixed solutions, copper sulphate and ferrous sulphate crystallise in the form of the latter. The alums also have the same crystalline form, but differ in chemical composition.

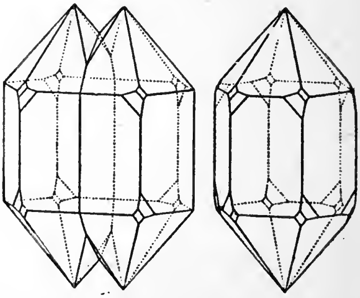


FIG. 254.—Twins of Right- and Left-handed Quartz. Partial and Complete Interpenetration.

Mitscherlich (1820) cleared up these contradictions by showing that phosphates and arsenates, when they were of similar composition and contained the same amount of water of crystallisation, had almost exactly the same crystalline form: *e.g.*,

$Na_2HPO_4 + 12H_2O$, **disodium hydrogen phosphate,**
$Na_2HAsO_4 + 12H_2O$, **disodium hydrogen arsenate,**

yield crystals of the same form. Haüy's first axiom was therefore disproved. In the case of the salts $NaH_2PO_4 + H_2O$ and $NaH_2AsO_4 + H_2O$ the ordinary crystalline forms were different, but the phosphate sometimes crystallised in a new form, identical with the common form of the arsenate. Mitscherlich also discovered the monoclinic variety of sulphur, showing that elements may have different crystalline forms. Thus, one substance may assume two distinct crystalline forms, and is then called **dimorphous**. If it assumes more than two forms it is called **polymorphous**. Haüy's second axiom was, therefore, disproved.

The capacity of different, but chemically similar, substances of crystallising in the same form was called **isomorphism** by Mitscherlich; substances crystallising in the same form are called **isomorphous.** Since, however, numerous analogous compounds of phosphorus and arsenic, for example, are isomorphous, the latter name came to be applied to the elements, arsenic and phosphorus, themselves. **Isomorphous elements** are those which form similarly crystallising compounds with the same elements or radicals: they can replace each other in their compounds without causing any essential alteration in the crystalline form. It is not necessary that the *free* elements shall have similar crystalline forms, although this is sometimes the case.

Mitscherlich at first considered that the same number of atoms combined in the same manner produce the same crystalline form, so that the latter is independent of the chemical nature of the atoms, and is determined solely by their number and mode of combination. This generalisation proved to be too wide, and it was found that an atom can be replaced by another without producing a change of form only when the elements are chemically analogous.

More accurate measurements of crystal angles have shown, as Mitscherlich conjectured, that the law is only approximate. Except in the regular system, the replacement of an atom of one element by an atom of an isomorphous element leads to a change in the crystal angles which may, it is true, be small, but may amount to several degrees. Haüy's first axiom is, therefore, correct in the strictest sense, although it is often only by refined measurements that differences in the angles of crystals which are almost exactly alike in appearance may be detected.

Thus, Tutton, in a long series of very exact measurements, found that the crystal angles in isomorphous sulphates and selenates of potassium, rubidium, and cæsium, changed slightly when one isomorphous element (K, Rb, Cs, or S, Se) was replaced by another. The change, which may be expressed in terms of the ratios of the lengths of the axes, *a, b, c,* depends in a regular manner on the atomic weight of the element.

K_2SO_4	$a : b : c = 0{\cdot}5727 : 1 : 0{\cdot}7418$	(K = 38·79)
Rb_2SO_4	$a : b : c = 0{\cdot}5723 : 1 : 0{\cdot}7485$	(Rb = 84·77)
Cs_2SO_4	$a : b : c = 0{\cdot}5712 : 1 : 0{\cdot}7531$	(Cs = 131·6).

The other properties of the crystal (molecular volume = $\frac{\text{molecular weight}}{\text{density}}$, refractive indices, coefficients of expansion, thermal conductivity) altered with the crystal angles, showing that the crystalline form is closely related to the nature of the atoms which make up the structure of the crystal.

Isomorphous elements.—As a result of the investigations of crystalline form, it has been possible to classify the elements into eleven groups, the members of each group being capable of replacing one another without sensible alteration of crystalline form. The members of each group are called **isomorphous elements.**

I. Cl, Br, I, F ; Mn (in permanganates, *e.g.*, $KMnO_4$ isomorphous with $KClO_4$).
II. S, Se ; Te (in tellurides) ; Cr, Mn, Te (in the compounds K_2RO_4) ; As and Sb in the glances MR_2.
III. As, Sb, Bi ; Te (element) ; P, V (in salts) ; N, P (in organic bases).
IV. K, Na, Cs, Rb, Li ; Tl, Ag.
V. Ca, Sr, Ba, Pb ; Fe, Zn, Mn, Mg ; Ni, Co, Cu ; Ce, La, Pr, Nd : Er, Y with Ca ; Cu, Hg with Pb ; Cd, Be, In with Zn ; Tl with Pb.
VI. Al, Fe, Cr, Mn ; Ce, U in oxides R_2O_3.
VII. Cu, Ag in compounds of lower oxides ; Au.
VIII. Pt, Ir, Pd, Rh, Ru, Os ; Au, Fe, Ni ; Sn, Te.
IX. C, Si, Ti, Zr, Th, Sn ; Fe, Ti.
X. Ta, Nb.
XI. Mo, W, Cr.

Several elements occur in more than one group. Thus, **chromium** occurs in VI with Al, Fe, etc., because of the isomorphism of the oxides R_2O_3, the spinels, $\overset{II}{R}\overset{III}{R'_2}O_4$, *e.g.*, MgO, Al_2O_3, or $\overset{II}{Mg}\overset{III}{Al_2}O_4$, FeO,Fe_2O_3, FeO,Cr_2O_3, etc., and the alums, *e.g.*, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, $K_2SO_4,Cr_2(SO_4)_3,24H_2O$, $K_2SO_4,Fe_2(SO_4)_3,24H_2O$. It occurs in group II because of the isomorphism of the salts K_2SO_4, K_2CrO_4, K_2MnO_4, etc. **Manganese** occurs in group V because of the isomorphism of the carbonates $CaCO_3$, $\overset{II}{Fe}CO_3$, $\overset{II}{Mn}CO_3$; in group VI because of the isomorphism of the spinels (containing $\overset{\mathrm{III}}{\mathrm{Mn}}_2\mathrm{O}_3$, $\overset{\mathrm{III}}{\mathrm{Fe}}_2\mathrm{O}_3$, etc.); in group II because of the isomorphism of $\mathrm{K}_2\overset{\mathrm{VI}}{\mathrm{Mn}}\mathrm{O}_4$ with $\mathrm{K}_2\overset{\mathrm{VI}}{\mathrm{S}}\mathrm{O}_4$, etc.; and in group I because of the isomorphism of $\mathrm{K}\overset{\mathrm{VII}}{\mathrm{Mn}}\mathrm{O}_4$ and $\mathrm{K}\overset{\mathrm{VII}}{\mathrm{Cl}}\mathrm{O}_4$. The close connection between the **valencies** of an element and its position in the groups of isomorphous elements is clear from the above, and from a comparison of the table of isomorphous elements with that of valencies (p. 252).

The **formulæ** of similar compounds may be deduced from their isomorphism: thus, from the fact that potassium selenate crystallises in the same form as potassium sulphate, Mitscherlich concluded that its formula must be K_2SeO_4, corresponding with K_2SO_4. From its composition the atomic weight of selenium could then be calculated.

Atomic weights from isomorphism.—The applications of isomorphism to the deduction of atomic weights are all based on the axiom that **isomorphous compounds have similar formulæ.**

Thus, ferric oxide, chromic oxide, and alumina are isomorphous, since mineral crystals of these compounds have the same form. The vapour density of aluminium chloride can be found, and corresponds with the formula $AlCl_3$. The formula of alumina will then be Al_2O_3. We therefore assume the formulæ Fe_2O_3 for ferric oxide and Cr_2O_3 for chromic oxide, and from the percentage compositions of these oxides the atomic weights of the metals may then be calculated. These are confirmed by the specific heats of the metals, which are 0·1146 and 0·104, respectively.

The best example of isomorphism is probably that studied by Roscoe in connection with the **atomic weight of vanadium.** The following minerals had the formulæ given assigned to them by Berzelius:

Apatite,	$3Ca_3(PO_4)_2 + CaF_2$, or $Ca_5P_3O_{12}F$
Pyromorphite,	$3Pb_3(PO_4)_2 + PbCl_2$, or $Pb_5P_3O_{12}Cl$
Mimetite,	$3Pb_3(AsO_4)_2 + PbCl_2$, or $Pb_5As_3O_{12}Cl$
Vanadinite,	$3Pb_3V_2O_6 + PbCl_2$, or $Pb_5V_3O_9Cl$.

In these formulæ, lead and calcium, and arsenic and phosphorus, replace each other, but the formula of vanadinite is quite different from those of the other compounds, although all the minerals crystallise in the same form. Roscoe therefore concluded either that the law of isomorphism was incorrect or that Berzelius was in error in attributing the above formula to vanadinite.

By reinvestigating the vanadium compounds, Roscoe was able to show that the substance regarded as metallic vanadium by Berzelius was really an oxide, VO. The formulæ of the minerals were now completely analogous:

Apatite,	$3Ca_3(PO_4)_2 + CaF_2$, or $Ca_5P_3O_{12}F$
Pyromorphite,	$3Pb_3(PO_4)_2 + PbCl_2$, or $Pb_5P_3O_{12}Cl$
Mimetite,	$3Pb_3(AsO_4)_2 + PbCl_2$, or $Pb_5As_3O_{12}Cl$
Vanadinite,	$3Pb_3(VO_4)_2 + PbCl_2$, or $Pb_5V_3O_{12}Cl$.

The atomic weight of vanadium found by Berzelius, 68·5, was, therefore, in reality the molecular weight of the oxide VO, and the true value was $68{\cdot}5 - 16 = 52{\cdot}5$. Roscoe then found that the vanadium compounds investigated by Berzelius contained phosphoric acid, which is exceedingly difficult to separate. By using pure compounds he found $V = 51{\cdot}4$.

Formulæ of minerals.—Since a certain amount of one element can be replaced in a compound by an equivalent amount of an isomorphous element, the formula of the compound calculated from its analysis will not usually give a whole number of atoms of each isomorphous element.

Thus, spathic iron ore, $FeCO_3$, may have the iron partly or completely ($MnCO_3$) replaced by the isomorphous element manganese. The relative proportions of the two metals may vary from Fe = 48·2 per cent. and Mn = 0, to Fe = 0 and Mn = 47·8 per cent.

Such an **isomorphous mixture** is represented by a formula such as $(Fe,Mn)CO_3$, the isomorphous elements being enclosed in brackets with a comma separating them, and behaving as an equivalent amount of one element. If follows from the law of isomorphism that the sum of the *atomic* proportions of Fe and Mn, combined with the group CO_3, must always be equal to unity.

Mixed crystals.—A very important property of isomorphous substances is their capacity of crystallising together from solutions so as to form *homogeneous* crystals containing the isomorphous substances in variable proportions. Although the crystals are perfectly homogeneous, they are usually known as **mixed crystals**; a more appropriate name is **solid solutions.** These are also formed when the substances separate from a fused state.

Thus, if chrome alum, $K_2SO_4,Cr_2(SO_4)_3,24H_2O$, and ordinary potash alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, which form deep purple and colourless octahedral crystals, respectively, are dissolved together in water and the solution is allowed to crystallise, octahedral crystals containing both alums separate, having colours varying from a very pale purple to deep purple according to the amount of chrome alum they contain,

Isomorphous compounds cannot, therefore, be separated in a state of purity by crystallisation, as is the case with salts of different chemical types, crystallising in different forms, such as potassium nitrate and sodium chloride (p. 564). It is found that substances which crystallise in the same form, but belong to different chemical types, do not form mixed crystals, or only to a very limited extent, whereas chemically analogous compounds may form mixed crystals even though the crystal angles differ by as much as 5° : the resulting crystals have angles which lie between those of the components.

Retgers (1889) considers the property of forming mixed crystals to be a very important **criterion of isomorphism.** He also considers that the variation in the physical properties of the mixed crystal with the proportion of its constituents is a valuable guide in deciding whether the substances are truly isomorphous or not. One of these physical properties is the **specific volume,** *i.e.*, the reciprocal of the density, or the volume in c.c. of 1 gram of the substance. If this is plotted against the proportions of the constituents, the points must, according to Retgers, lie on a straight line which shows no change of direction anywhere. The substances may be only **partially miscible,** in which case there is a gap in the line, but if the substances are isomorphous one part of the line is a continuation of the other, and there is no change of direction.

Overgrowth crystals.—If an octahedral crystal of chrome alum is suspended by a thread in a saturated solution of potash alum, a colourless overgrowth of the latter salt is deposited on the violet crystal as a nucleus. In the same way, a green crystal of nickel sulphate, $NiSO_4,7H_2O$, may be covered with colourless zinc sulphate, $ZnSO_4,7H_2O$. H. Kopp (1879) regarded the property of forming **overgrowth crystals** as characteristic of isomorphous substances, but exceptions to this criterion are known ; thus, rhombic K_2SO_4 (pseudo-hexagonal) may form an overgrowth of hexagonal $KNaSO_4$.

Exceptions to the law of isomorphism.—Exceptions to the law of isomorphism are frequent. In some cases this may be due to the existence of two or more varieties of a substance—**dimorphism,** or **polymorphism,** respectively, only one of which, not the common form, is isomorphous with the commonly occurring variety of a chemically similar substance. An example of this was discovered by Mitscherlich, viz., the acid phosphate and the acid arsenate of sodium : NaH_2PO_4,H_2O and NaH_2AsO_4,H_2O (p. 443). In many cases, however, isomorphism is observed with substances exhibiting no chemical similarities. Thus, the ammonium salts, containing the radical NH_4, are isomorphous with potassium and sodium salts containing the atoms K and Na ; silver sulphide, Ag_2S, in the mineral *argentite* is isomorphous with lead sulphide in *galena*, PbS, the two forming mixed crystals ; calcium carbonate, $CaCO_3$, occurs in the same form (*aragonite*) as sodium nitrate, $NaNO_3$; the compounds Mg_2SiO_4 and Al_2BeO_4 are isomorphous ; and so on.

Other examples of isomorphism without similarity in chemical composition are shown in the following groups :

(1) Potassium periodate, KIO_4
Calcium tungstate, $CaWO_4$
Potassium osmiamate, $KOsO_3N$

(2) Potassium sulphate, K_2SO_4
Potassium beryllium fluoride, K_2BeF_4

(3) Potassium perchlorate, $KClO_4$
Barium sulphate, $BaSO_4$
Potassium borofluoride, KBF_4

(4) Yttrium phosphate, YPO_4
Zircon, $ZrSiO_4$
Tinstone, SnO_2, or $SnSnO_4$.

In these groups the molecule contains the same number of atoms, and the original idea of Mitscherlich, that the form depended on the number of atoms in the molecule, and not on their chemical nature, is verified.

These exceptions to the law of isomorphism, although of great interest to crystallography, have little significance in the chemical application of the law ; the latter has served its purpose, and has led to the correction of some atomic weights which have been confirmed by more certain methods. There remains no possibility that these numbers will ever be modified as a result of further compilation of lists of exceptions to the law of isomorphism, and the latter have no further interest to chemists.

EXERCISES ON CHAPTER XXIII

1. What methods are used in deciding which multiple of the equivalent is the atomic weight of an element ? The composition of potassium selenate, as determined by Mitscherlich, is : potassium 35·29 ; selenium 35·75 ; oxygen 28·96. The salt is isomorphous with potassium sulphate, K_2SO_4. Find the atomic weight of selenium.

2. The vapour density of aluminium bromide is 268 ($H = 1$). Its percentage composition is : aluminium = 10·15 ; bromine = 89·85. The specific heat of aluminium is 0·225. Find the atomic weight of aluminium.

3. State Dulong and Petit's law. With what degree of exactness does it hold, and what modifications of it have been proposed ?

4. What is known as to the atomic heats of elements at low temperatures ?

5. What relation exists between the molecular heat of a solid compound and the atomic heats of its constituents ? The specific heat of nickel sulphide (NiS) is 0·1281. The specific heat of nickel is 0·1092 ; find the specific heat of sulphur.

6. The specific heat of anhydrous calcium chloride is 0·1675, that of the hexahydrate is 0·3461. Find the specific heat of the water of crystallisation, and compare the number with the specific heat of ice (p. 201).

7. What do you understand by a " crystal " ? What elements of symmetry are met with in crystals ?

8. What are the crystal systems? To what systems do the following belong: rock salt, alum, potassium dichromate, blue vitriol, calcite, borax?

9. Explain the meaning of: axis of symmetry, pinakoid, hemihedral form, macrodome, twin crystal, dimorphism, isomorphous element.

10. What are the criteria of isomorphism? What exceptions to the law of isomorphism are met with?

11. A mineral has the following percentage composition: Fe = 28·6; Mn = 19·5; CO_3 = 51·9. Find its formula.

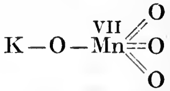
CHAPTER XXIV

THE CLASSIFICATION OF THE ELEMENTS AND THE PERIODIC LAW

Classification of the elements.—In **classification,** things are grouped according to **similarity ;** those which resemble one another in some respects being placed together, and those which are dissimilar being separated.

Various criteria of likeness may be adopted, and it frequently happens that things grouped according to one kind of likeness are separated on the basis of another. The best classification will be that in which the things grouped together in it resemble one another in the greatest possible number of respects, each of which might itself serve as the basis of a separate, and more specific, classification.

The classification of the elements into **metals** and **non-metals** is one obvious basis, although it presents certain difficulties. The differences between metals and non-metals are in fact not always sharply defined : the following are usually accepted as the most important :—

METALS are **electropositive elements** (*cf.* p. 252) ; they normally give **basic oxides** [acidic oxides are only formed when the atom has higher valencies, *e.g.*, $\overset{\mathrm{II}}{\mathrm{Mn}}=\mathrm{O}$ (*basic*) ;  $\mathrm{K-O-\overset{VII}{Mn}}\begin{smallmatrix}\diagup \mathrm{O}\\ = \mathrm{O}\\ \diagdown \mathrm{O}\end{smallmatrix}$ (acidic)] ; they form **halogen compounds stable in presence of water** (KCl, $PbCl_2$), or decomposed only to a limited extent ($BiCl_3$, $SbCl_3$), the reaction being reversible, $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$; they form **complex salts,** in which the metal may be present either in the electropositive radical (cation), as in $[Ag(NH_3)_2]Cl$, or in the electronegative radical (anion), as in $K[AgC_2N_2]$.

NON-METALS are either **electronegative elements,** or show only very feeble electrochemical properties (*e.g.*, carbon) ; they give **acidic oxides** in which the element has its normal valency (in some cases metallic oxides with normal valency can function as feebly acidic oxides in the presence of a strong base ; *e.g.*, zinc oxide, ZnO, can give a stable chloride, $ZnCl_2$, with hydrochloric acid, or an unstable zincate, $Zn(ONa)_2$, with caustic soda); their **halogen compounds** are almost completely **decomposed by water**: $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$.

Certain **physical properties** commonly supposed to be characteristic of **metals** are not so in reality:

lustre: this is shown by the non-metals iodine and carbon (graphite);

malleability: some metals (*e.g.*, Bi, Sb) are brittle; plastic sulphur may be regarded as a malleable non-metal;

high density: the alkali-metals are lighter than water (*e.g.*, Li, sp. gr. 0·53), iodine has a density of 4·9;

conductivity for heat and electricity: graphite is a good conductor of electricity, whilst some metals are relatively poor conductors, *e.g.*, bismuth.

The classification of elements according to **valency** (*cf.* p. 252) is not entirely satisfactory for two reasons: (1) the valency of some elements is variable; (2) elements having the same valency often differ in nearly every other respect (*e.g.*, sodium is a strongly electropositive metal; chlorine is a strongly electronegative non-metal; both are univalent elements).

The most satisfactory system of classification, and the one now adopted, is based on the relation between the properties of the elements and their **atomic weights.**

As early as 1817 Döbereiner noticed regularities in the atomic weights of elements which were chemically analogous. In groups of three such elements, the atomic weight of the middle element is approximately the mean of the atomic weights of the extreme elements. This is known as the **law of triads.** Thus in the following groups (H = 1) this is observed:

$$80{\cdot}54 \left\langle \begin{matrix} \text{Cl } 35{\cdot}18 \\ \text{I } 125{\cdot}91 \end{matrix} \right. \quad \text{Br } 79{\cdot}29\text{;} \quad 79{\cdot}16 \left\langle \begin{matrix} \text{S } 31{\cdot}81 \\ \text{Te } 126{\cdot}5 \end{matrix} \right. \quad \text{Se } 78{\cdot}6\text{;}$$

$$88{\cdot}01 \left\langle \begin{matrix} \text{Ca } 39{\cdot}75 \\ \text{Ba } 136{\cdot}28 \end{matrix} \right. \quad \text{Sr } 86{\cdot}93$$

Similar regularities were pointed out by Dumas, Pettenkofer, Odling, and other chemists, but little additional progress was made until a uniform set of atomic weights had been derived by Cannizzaro (1858) from Avogadro's law, and the law of atomic heats. So long as "equivalents," deduced from various considerations which had no real bearing on the matter, continued to be used by different chemists, no regularities could ever come to light.

Newlands published a series of papers in the *Chemical News*, beginning in 1863, in which he observed that if the new atomic weights are used, and if the elements are arranged in *the order of atomic weights*, "the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music." He called this the **law of octaves.**

1 H	2 Li	3 Be	4 B	5 C	6 N	7 O
8 F	9 Na	10 Mg	11 Al	12 Si	13 P	14 S
15 Cl	16 K	17 Ca	18 Cr	19 Ti	20 Mn	21 Fe, etc.

This relationship, which is based on what is now called the **atomic numbers** of the elements, was not wholly satisfactory, as can be seen.

MENDELÉEFF.

It was received with coolness by the London Chemical Society, which declined to publish Newlands's paper in its journal.

Although the germ of one of the most important chemical laws is contained in this table, the credit of having stated clearly the connection between the properties of the elements and their atomic weights, of forcing this result on the attention of contemporary chemists, and of making it the foundation of a comprehensive system of classification, belongs without question to the great Russian chemist, Dmitrij Ivanovitsch Mendeléeff (1834–1907), born at Tobolsk in Siberia, and professor at St. Petersburg from 1866 to 1890. Whilst engaged in writing his classical "Principles of Chemistry" (1st edition, 1869; 3rd English edition, 1905) Mendeléeff had ample opportunity of studying the properties of the elements, and during that period an idea arose in his mind, which, unlike the majority of ideas occurring to investigators, turned out to be a fundamental law.

The Periodic Law.—The basic idea of Mendeléeff's system of classification was that "there must be some bond of union between mass and the chemical elements; and as the mass of a substance is ultimately expressed in the atom, a fundamental dependence should exist and be discoverable between the individual properties of the elements and their atomic weights. But nothing, from mushrooms to scientific dependence, can be discovered without looking and trying. So I began to look about and write down the elements with their atomic weights and typical properties, analogous elements, and like atomic weights on separate cards, and this soon convinced me that **the properties of the elements are in periodic dependence upon their atomic weights**; and although I have had my doubts about some obscure points, yet I have never once doubted the universality of this law, because it could not possibly be the result of chance." ("Principles of Chemistry," II, p. 30, 1905.) Immediately after the publication of this **Periodic Law** by Mendeléeff in 1869, an identical generalisation was put forward independently by Lothar Meyer in 1870.

Mendeléeff from the first was convinced of the accuracy of the law, and did not hesitate to alter some of the accepted atomic weights on that ground: Lothar Meyer was doubtful, believing that "it would be rash to change the accepted atomic weights on the basis of so uncertain a starting point." Further work has, with one doubtful exception (tellurium), confirmed the changes boldly advocated by the Russian chemist.

The essence of the Periodic Law is contained in Mendeléeff's statement, quoted above. As the atomic weights progressively increase, the properties of the elements alternately ebb and flow. The heights of the tide, the alternation of day and night, and of the seasons, are in the same way in periodic dependence on the uniform march of time, the fundamental independent variable.

Atomic volumes.—In testing the Periodic Law it is desirable to use such properties of the elements as can be expressed numerically. One of these is the **atomic volume,** *i.e.*, the volume in c.c. of the atomic weight in grams of a *solid* element, or in other words the atomic weight divided by the density :

$$\text{Atomic volume} = \frac{\text{Atomic weight}}{\text{Density}} = \frac{A}{D}.$$

These atomic volumes represent, not the space occupied by the atoms themselves, but this plus the empty spaces between the atoms in the material. If the atoms are assumed to be spherical, $\sqrt[3]{A/D}$ is a measure of the mean distance between the atomic centres.

The atomic volumes of a few important elements are given below.

Element.	At. wt. (H = 1)	Density at 15°	Atomic volume.
Hydrogen	1	0·086 at −250°	11·6
Lithium	6·9	0·534	12·9
Sodium	22·8	0·971	23·5
Potassium ...	38·8	0·862	45·0
Rubidium... ...	84·8	1·532	55·2
Cæsium	131·8	1·87	70·5
Calcium	39·8	1·55	25·7
Strontium ...	87·0	2·54	34·3
Barium	136·3	3·75	36·4
Chlorine	35·2	2·49 (liq. at 0°)	14·1
Bromine	79·3	3·102 (25°)	25·5
Iodine	126·0	4·95	25·5
Iron	55·4	7·86	7·05
Lead	205·5	11·37	18·1

Mendeléeff remarked that comparatively light and reactive elements have the largest atomic volumes (Na, K, Rb, Cs, halogens); elements which are not very reactive have small atomic volumes (C as diamond, Ni, Co, Ir, Pt). Lothar Meyer plotted the atomic volumes against the atomic weights, and obtained the **atomic volume curve** shown in Fig. 255. This curve also exhibits periodicity in the case of other properties, such as expansion by heat, conductivity for heat and electricity, magnetic susceptibility, melting point, refractive index, boiling point, crystalline form, compressibility, atomic heat (plotted as the thin curve in Fig. 255), heats of formation of oxides and chlorides, hardness, malleability, volatility, volume change on fusion, viscosity and colour of salts in aqueous solution, mobilities of ions (p. 288), electrode potentials of metals (p. 884), over-voltage of metals, frequency of atomic vibrations in solids (p. 430), distribution of the elements in nature (p. 32), distribution of lines in spectra (p. 756), and valency.

As Mendeléeff said, "these regularities can hardly be the result of chance."

Lothar Meyer pointed out that ductile metals of low density occupy the maxima (Li, Na, K, Rb, Cs), or descending parts of the curve near the maxima (Mg, Ca, Sr, Ba). Ductile metals of high density occupy the minima (Al, Fe, Ru, Ce, Ir), and adjacent parts of the ascending curves (Ni, Cu, Pd, Ag, Pt, Au). Brittle metals of high density occur on the descending parts of the curve shortly before the minima (Ti, V, Cr, Mn, Sb, Bi : exceptions are Ta, W, Ir.)

Fusibility and volatility.—The fusibility and volatility of elements, given by their melting and boiling points, are also in periodic dependence on the atomic weights. All the gaseous elements and those fusing readily below a red heat (see table), occur at the maxima and on ascending portions of the atomic volume curve. Difficultly fusible elements occur at the minima or on descending portions of the curve.

Carnelly found a similar periodic dependence of the melting points of the metallic chlorides, and the heats of formation of the oxides and chlorides, on the atomic weight of the metal : the periodicity of properties thus extends to the **compounds** of elements.

Electrochemical character.—The electrochemical character of an element, which will be more closely considered later (p. 886), is roughly defined by the chemical character of its oxide : **electropositive elements** yield **basic oxides** (p. 450), whilst **electronegative elements** yield **acidic oxides.** If the part of the atomic volume curve situated between two maxima is called a **section**, then all elements on descending parts of the second and third sections are electropositive ; those on ascending portions are electronegative. Elements situated on sections 4 and 5 exhibit electrochemical properties passing through two periods whilst the atomic volumes pass through only one. On the first portion of the descending curve of each of these sections, strongly electropositive elements occur (K, Ca ; Rb, Sr) ; these are followed, on the same part of the curve, by more or less electronegative elements (V, Cr, Mn ; Zr, Nb, Mo, Ru, Rh), which are again followed, on the ascending portions of the curve, by electropositive elements (Fe, Ni, Co, Cu, Zn, Ga ; Pd, Ag, Cd, In) ; finally, after these on the same but higher parts of the curve, come electronegative elements (As, Se, Br ; Sn, Sb, Te, I). The sixth and seventh sections are considerably broken up, but similar regularities are noticed.

Atomic heats.—The **atomic heats** of solid elements are, at the ordinary temperature, practically constant and equal to 6·3. The curve representing them on the atomic weight diagram is therefore a horizontal straight line. It was formerly considered that the atomic (or the specific) heat was an exceptional property with respect to periodicity: the more accurate investigations of Dewar at low temperatures (1913) showed, however, that the atomic heats at low temperatures, when plotted in terms of the atomic weights, reveal definitely a periodic variation closely resembling the atomic volume curve. The similarity of the two curves suggests that, at low temperatures, equal *volumes* of different elements, instead of equal numbers of atoms, have the same capacity for heat (Fig. 255).

Compressibilities.—Since the **compressibilities** of solid elements are in periodic dependence on the atomic weights, T. W. Richards supposes that this indicates that the atoms themselves are compressible. It is very improbable that such a conclusion is justified in the sense understood by Richards. It is more likely that the atomic forces, which resist the approach of atoms situated at small distances from each other, are dependent on the masses of the atoms, or their electrical constitution, in a periodic manner.

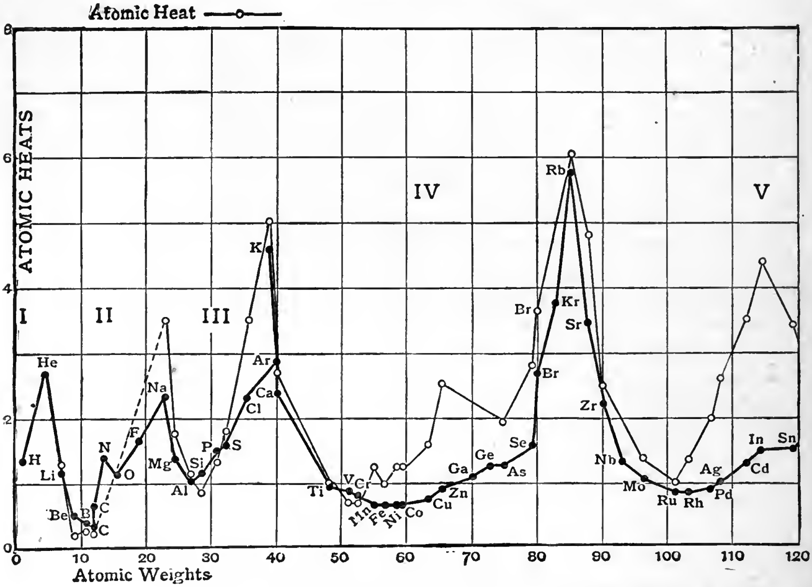


FIG. 255.—Dewar's Atomic Heat Curve with a Curve of Atomic Volumes.

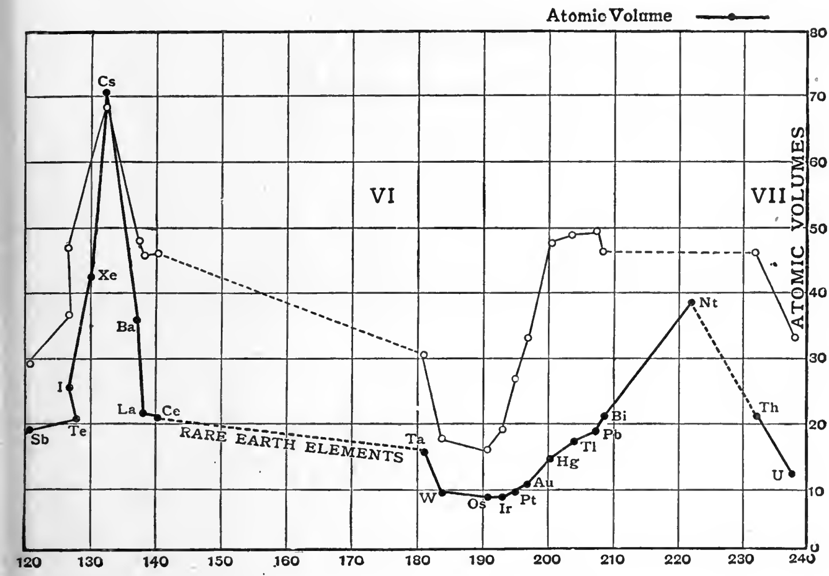
The periodic law.—The original statement of Mendeléeff (1869) includes practically the whole content of the **Periodic Law.** It is given in eight paragraphs :

"(1) The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

"(2) Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (platinum, iridium, osmium), or which increase regularly (potassium, rubidium, cæsium).

"(3) The arrangement of the elements, or of groups of elements, in the order of their atomic weights corresponds with their so-called *valencies*.

"(4) The elements which are the most widely distributed in nature have *small* atomic weights, and . . . sharply defined properties. They are therefore typical elements.



(*From Lowry*: "*Historical Introduction to Chemistry*," *Macmillan*.)

"(5) The *magnitude* of the atomic weight determines the character of an element [and those of its compounds.]

"(6) The discovery of many yet unknown elements may be expected, for instance elements analogous to aluminium and silicon, whose atomic weights would be between 65 and 75. [These have since been discovered.]

"(7) The atomic weight of an element may sometimes be corrected by the aid of a knowledge of those of the adjacent elements. [This has been done in several cases.]

MELTING AND BOILING POINTS OF THE CHEMICAL ELEMENTS (in degrees C.)

Element.	M.-pt.	B.-pt.	Element.	M.-pt.	B.-pt.	Element.	M.-pt.	B.-pt.
Helium	< −271	−268·8	Tin	231·9	2270	Samarium	1300–1400	—
Hydrogen	−259	−252·7	Bismuth	271	1420	Silicon	1420	3500?
Neon	−253?	−239	Thallium	302	1280?	Nickel	1452	2330?
Fluorine	−223	−187	Cadmium	320·9	778	Cobalt	1480	—
Oxygen	−218	−182·9	Lead	327·4	1525	Yttrium	1490	—
Nitrogen	−210	−195·7	Zinc	419·4	918	Iron	1530	2450
Argon	−188	−186	Tellurium	452	1390	Palladium	1549	2540
Krypton	−169	−151·7	Antimony	630·0	1440	Chromium	1615	2200
Xenon	−140	−109	Cerium	640	—	Zirconium	1700?	—
Chlorine	−101·5	− 33·6	Magnesium	651	1120	Niobium	1950	—
Mercury	− 38·87	356·7	Aluminium	658·7	1800	Thorium	1450	—
Bromine	− 7·3	63	Radium	700	—	Vanadium	1720	—
Cæsium	+ 26	670	Calcium	810	—	Platinum	1755	2450?
Gallium	30	—	Lanthanum	810?	—	Titanium	1800	—
Rubidium	38	696	Strontium	> 900?	—	Uranium	< 1850	—
Phosphorus	44	287	Neodymium	840?	—	Rhodium	1950	2500?
Potassium	62·04	758	Arsenic	850	subl. 450.	Boron	2200–2500?	3500?
Sodium	97·6	877	Barium	850	—	Iridium	2350?	2550?
Iodine	113·5	184·4	Praseodymium	940	—	Ruthenium	2450?	2520?
Sulphur	S_I 112·8	444·55	Germanium	958	—	Molybdenum	2550	3200?
	S_{II} 119·2		Silver	960·5	1955	Osmium	2700?	—
	S_{III} 106·8		Gold	1063·0	2530?	Tantalum	2900	—
Indium	155	1000?	Copper	1083·0	2310	Tungsten	3400	3700?
Lithium	180·1	> 1400	Manganese	1230	1900	Carbon	> 3600	—
Selenium	217–220	690	Beryllium	1280	—			

"(8) Certain characteristic properties of the elements can be foretold from their atomic weights." [*Cf.* (6).]

The periodic system : Mendeléeff arranged the elements in a table, called the **periodic table,** or **periodic system,** an abbreviated form of which is given below. In this the elements are arranged in nine vertical columns, called **groups,** headed by zero (0) and the Roman numerals from I to VIII. These groups arise by suitably breaking up, into assemblages, a continuous series of the elements arranged in the order of their atomic weights. These assemblages are called **periods,** and if the periods are written one beneath the other in horizontal rows, the elements of all the periods which are vertically beneath each element in the first period constitute the groups. The first complete period contains eight elements, from helium to fluorine ; the next period also contains eight elements, from neon to chlorine, and elements of the second period are analogous to those vertically above them in the first period. In other words, the periodicity of properties begins again after fluorine, and the same types of properties are met with in the ninth, tenth, eleventh, etc., elements, as in the first, second, third, etc.

PERIODIC TABLE.

PERIOD.	SERIES.	GROUP.								
		0.	I.	II.	III.	IV.	V.	VI.	VII.	
1	1		H							
	2	He	Li	Be	B	C	N	O	F	
2	3	Ne	Na	Mg	Al	Si	P	S	Cl	VIII.
3	4	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni
	5		Cu	Zn	Ga	Ge	As	Se	Br	
4	6	Kr	Rb	Sr	Y	Zr	Nb	Mo	—	Ru Rh Pd
	7		Ag	Cd	In	Sn	Sb	Te	I	
5	8	Xe	Cs	Ba	15 Rare Earths	Ce	Ta	W	—	Os Ir Pt
	9		Au	Hg	Tl	Pb	Bi	—	—	
6	10	Nt	—	Ra	—	Th	—	U	—	

After chlorine, however, eleven elements, instead of eight, must be passed over before the periodic recurrence of properties begins again. At the beginning of this period we also meet with the first serious difficulty in the periodic system, viz., that the element next in atomic weight to chlorine is potassium, which undoubtedly belongs to the same group as sodium. The next element is argon, which is an inert gas resembling helium and neon, and therefore belonging to the zero group. The order of the two elements in respect of their atomic weights is therefore the inverse of the order in the periodic system which brings them into the same groups as their chemical analogues. In such cases, where the atomic weights are apparently inverted, the elements are placed in the groups to which they naturally belong, and the atomic weights disregarded. Three such pairs of elements are known (H = 1):

1. A 39·6; K 38·8. 2. Co 58·50; Ni 58·21.
3. Te 126·5; I 125·91.

With this transposition of argon and potassium, the natural sequence runs along the period until manganese is reached. We should then expect an inert element resembling argon. Actually we encounter three elements, iron, cobalt, and nickel, with atomic weights almost identical, and resembling one another very closely in their physical and chemical properties. After these three elements come copper, zinc, etc., which resemble in some respects the elements of Groups I, II, etc., and the inactive element does not appear. The three elements iron, cobalt, and nickel are placed in a separate group, viz., Group VIII, no representatives of which exist in the preceding periods, and the elements following, viz., copper, zinc, etc., which do not closely resemble the preceding elements of the same groups, are separated from these by placing them on the right in the group, whilst the other elements are placed on the left.

The three elements in Group VIII belonging to this period are called **transitional elements,** and instead of two **short periods** of eight elements in each, the whole of the 18 elements from argon to bromine, inclusive, are regarded as forming a **long period,** divided into elements belonging to **even** and **odd** series according as they occur in series of even (*e.g.*, Ca) or odd (*e.g.*, Cu) number, beginning with hydrogen.

This first long period is followed, after bromine, by a second long period, beginning with the inactive element krypton, followed by the odd elements of the period as far as molybdenum. These elements resemble the corresponding odd elements of the preceding long period. But after molybdenum we should expect an element resembling manganese. Instead of this, we find a cluster of three elements with very similar atomic weights, and with closely allied chemical properties, viz., ruthenium, rhodium, and palladium. These obviously are transitional elements, of the same type as iron, cobalt, and nickel, and must therefore be placed in Group VIII. This leaves a gap in Group VII, which we must assume should be occupied by a **missing**

element, not yet discovered, which should resemble manganese. The even elements of the long period then follow, ending with iodine.

At this point there is a repetition of the inversion of atomic weights previously met with in the case of argon and potassium. Iodine is undoubtedly a halogen element, belonging to Group VII, whilst tellurium is equally certainly an element of Group VI, which contains its chemical analogues, sulphur and selenium. In the order of atomic weights, however, the positions would be reversed. Again we disregard the atomic weights and place the two elements in those positions which are in conformity with their chemical properties.

A new period begins with xenon, and proceeds as far as lanthanum, in Group III, in a regular manner. After lanthanum, however, comes a series of thirteen elements, with atomic weights differing by one or two, or even four, units, all of which are most closely analogous in chemical properties, and very difficult to separate in analysis. These are the elements of the **rare earths.** Two elements of the rare earths, viz., scandium and yttrium, occur in previous periods; it is obviously impossible to proceed in the normal manner with the fourteen elements now encountered:

La	Ce	Pr	Nd	—	Sa	Eu	Gd	Tb	Dy	Ho	Er
138·0	139·2	140·0	143·2	—	149·3	150·9	156·1	158·0	161·3	162·3	166·4

$$\underbrace{\mathrm{Tm}_1\quad\mathrm{Tm}_2}_{167\cdot 2}\qquad\begin{array}{c}\mathrm{Yb}\\ 172\cdot 2\end{array}\qquad\begin{array}{c}\mathrm{Lu}\\ 173\cdot 7\end{array}$$

In this case, instead of one element occupying a place in the group in the normal manner, we encounter a cluster of fourteen. These must be placed in the same group as scandium and yttrium; the regular periodic change in the properties of the elements is checked at this point, and goes forward again only when the atomic weight has increased by about 40 units.

After the rare-earth elements the table becomes, apparently, somewhat incomplete (see the full table on p. 466). From the chemical properties of its quadrivalent compounds, cerium is usually placed in Group IV. After cerium the next element is tantalum, with an atomic weight about six units higher than lutecium, the last element of the rare-earth group. It may therefore be inferred, since the average difference of atomic weights of successive elements in this period is about three units, that an unknown element of the rare earths should come between lutecium and tantalum, and occupy Group III, since cerium is given the place in Group IV, and tantalum is, from its chemical characteristics, obviously an element of Group V. After tantalum comes tungsten, then three transitional elements: osmium, iridium, and platinum, which fall in Group VIII, leaving a blank for an unknown element in Group VII. The rest of this long period is continued

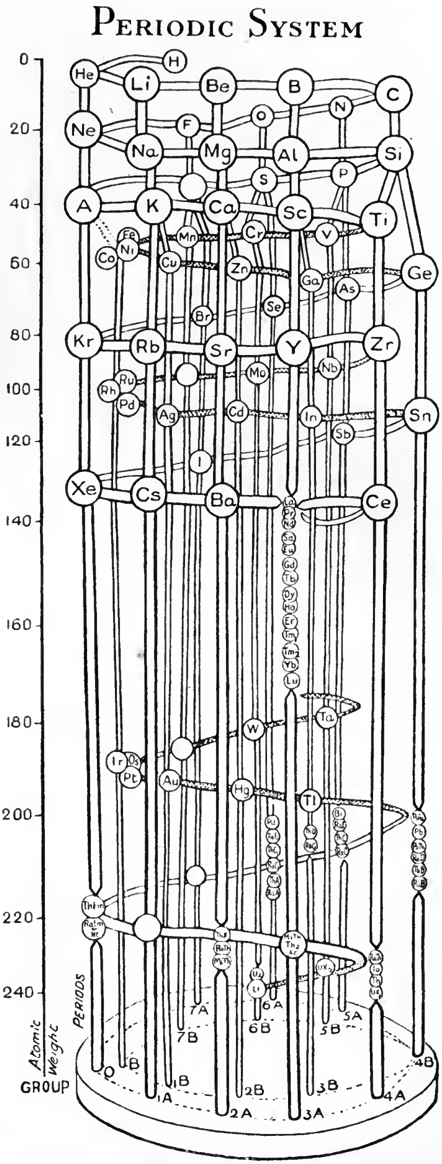


FIG. 256.—Arrangement of Elements in Periodic System according to Harkins and Hall.

from gold, in Group I, to bismuth, in Group V. The final period contains radioactive elements. In this part of the periodic table a very remarkable circumstance has lately come to light, viz., that one place can be occupied by a group of elements having very nearly the same atomic weights, and chemically inseparable: these elements are called **isotopes** (p. 114). Thus, the position marked "Pb" (lead) in the table is in reality occupied by *ten* elements, some of which are products of radioactive changes, as will be explained later, all chemically inseparable but having different atomic weights:

	Atomic weight (H = 1
1. Lead from radium ...	204·5
2. Ordinary lead	205·6
3. Lead from thorium ...	206·5
4. Radium D	208·4
5. Thorium B	212·4
6. Radium B	210·4
7. Lead from actinium ...	?
8. Lead from actinium B	?
9. Product of branch-chain, radium series	208·4
10. Product of branch-chain, actinium series	?

A similar state of affairs is found in the place occupied by bismuth, which includes ordinary bismuth, radium C, radium E, actinium C, and thorium C; and also in other positions.

The close resemblance of elements occupying odd or even periods, and their difference from elements of even or odd periods, respectively, in the same group, has been mentioned. Thus, the odd series in Group VI comprises Cr, Mo, W, U, and the even series S, Se, Te. It is only elements taken from an odd *or* even series in a group which obey the law of triads (*e.g.*, Ca, Sr, Ba; *or* Zn, Cd, Hg, in Group II).

Several space-models of the periodic system have been devised: the latest is that due to Harkins and Hall (1915), which is shown in Fig. 256. It consists of a double spiral, and the relationships between the elements are readily seen.

The periodicity of valency.—Mendeléeff in his original statement of the Periodic Law (p. 457) pointed out that the number of the group in the system corresponds with the **valency** of the elements occurring in it. In some cases (*e.g.*, N, S, Cr, Mn, Fe, etc.) it is necessary to attribute to an element its maximum valency, in others (Cu, Ag, Au) the minimum valency, and the assignment of valency therefore seems a little artificial. This has been urged as a defect of the periodic system by Wyruboff (1896), but if we keep in mind how little is really known of valency, the discrepancies are not serious. The valencies are most clearly seen in the different groups when **oxygen compounds** are considered:

Group

I	II	III	IV	V	VI	VII	VIII
Li_2O	(Be_2O_2)	B_2O_3	(C_2O_4)	N_2O_5	—	—	—
Na_2O	(Mg_2O_2)	Al_2O_3	(Si_2O_4)	P_2O_5	(S_2O_6)	Cl_2O_7	—
K_2O	(Ca_2O_2)	Se_2O_3	(Ti_2O_4)	V_2O_5	(Cr_2O_6)	[Mn_2O_7]	—
Cu_2O	(Zn_2O_2)	Ga_2O_3	(Ge_2O_4)	As_2O_5	(Se_2O_6)	[Br_2O_7?]	—
Rb_2O	(Sr_2O_2)	Y_2O_3	(Zr_2O_4)	Nb_2O_5	(Mo_2O_6)	—	(Ru_2O_8)
Ag_2O	(Cd_2O_2)	In_2O_3	(Sn_2O_4)	Sb_2O_5	(Te_2O_6)	[I_2O_7]	—
Cs_2O	(Ba_2O_2)	La_2O_3	(Ce_2O_4)	Ta_2O_5	(W_2O_6)	—	(Os_2O_8)
Au_2O	(Hg_2O_2)	Tl_2O_3	(Pb_2O_4)	Bi_2O_5	(U_2O_6)	—	—

The inactive gases, which form no compounds and have therefore zero valency, occupy the zero group. This group separates the intensely electronegative elements of Group VII from the intensely electropositive elements of Group I. The transitional elements of Group VIII perform this function for the three parts of long periods where there is no inactive element. In these cases, however, the negative and positive properties of the elements in the first and seventh groups are much less marked than in the cases where inactive elements are interposed :

$$\overset{-}{\mathrm{F}}\ \mathrm{Ne}\ \overset{+}{\mathrm{Na}}\,;\ \overset{-}{\mathrm{Cl}}\ \mathrm{A}\ \overset{+}{\mathrm{K}}\,;\ \overset{-}{\mathrm{Mn}}\ (\mathrm{Fe, Co, Ni})\ \overset{+}{\mathrm{Cu}}\,;\ \overset{-}{\mathrm{Br}}\ \mathrm{Kr}\ \overset{+}{\mathrm{Rb}}\,;$$

$$\overset{-}{\mathrm{Mo}}\ (\mathrm{Ru, Rh, Pd})\ \overset{+}{\mathrm{Ag}}\,;\ \overset{-}{\mathrm{I}}\ \mathrm{Xe}\ \overset{+}{\mathrm{Cs}}\,;\ \overset{-}{\mathrm{W}}\ (\mathrm{Os, Ir, Pt})\ \mathrm{Au}.$$

An important distinction between elements of the odd and even series is the capacity of the former alone to form **organo-metallic compounds,** *i.e.*, compounds of metals (sometimes of non-metals closely related to metals, *e.g.*, boron) with hydrocarbon or other similar radicals, *e.g.*, $NaCH_3$, $Zn(C_2H_5)_2$, $Pb(C_2H_5)_4$. These are not formed by elements of the even series except of Group VIII.

The elements of Group VIII are distinguished by the facility with which they form **complex compounds,** especially those containing cyanogen or ammonia : potassium ferrocyanide, $K_4[FeCy_6]$; hexammine cobaltichloride, $[Co(NH_3)_6]Cl_3$.

Electrochemical character.—The strongly electropositive elements are associated towards the left of the table, beginning with Group I ; the elements of strongly electronegative character occur on the right of the table, the most marked being in Group VII. In passing along the period from Group I to Group VII the electropositive character diminishes. When Group IV is reached the elements show hardly any electrochemical character, either positive or negative, and are practically neutral. The electropositive character then changes over into electronegative, which becomes increasingly stronger until it reaches a maximum in Group VII. The electrochemical character is well shown in the oxides of elements of the second period :

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
strongly basic	basic	weakly basic and acidic	weakly acidic	fairly strongly acidic	strongly acidic	very strongly acidic

The gradation of electrochemical character is shown also in the groups themselves.

The last members of the even series resemble in many respects the first members of the next odd series (excluding the zero group). Thus, there is a gradual transition from chromium and manganese to copper and zinc, apart from the bridge formed by the transitional elements. This gradation of properties in the *periods* was insisted upon by Mendeléeff, but has been somewhat neglected in comparison with the more obvious gradations in the *groups*.

Differences between atomic weights.—The differences between the atomic weights of successive elements in the various periods show many striking regularities, which have been the object of interesting speculations. The earliest of these, dating back to

1815, long before the discovery of the periodic relationship, is **Prout's hypothesis.** According to this, **the atomic weights of the elements are whole multiples of that of hydrogen.** In 1816 Prout stated that the simplest explanation of this supposed regularity is to be found in the assumption that the atoms of all elements are formed by the condensation of a greater or smaller number of atoms of hydrogen, this element being the **primary matter** or **protyle** (Greek *prote*, first; *hule*, stuff, *cf*. p. 28).

Prout's hypothesis, although disproved in its original form by the accurate determinations of atomic weights made by Berzelius, still had an extraordinary fascination for chemists. When Dumas and Stas in 1841 redetermined the atomic weight of carbon, finding it almost exactly 12, and showing that Berzelius had made an error in this case of no less than 2·5 per cent., the figures of the latter were looked upon with great mistrust, which subsequent work has not justified. When, further, these two experimenters found that the atomic weight of oxygen was almost exactly 16, interest in Prout's hypothesis revived. The atomic weight of chlorine, however, was found to be nearly 35·5, so that Dumas suggested that atomic weights are multiples of **half** the atomic weight of hydrogen. Marignac (1860) suggested that the law of constant proportions might not be quite exact, but that small variations of composition might occur, which would explain the deviations from whole numbers. Stas, beginning with "an almost complete confidence in the exactness of the law of Prout," was led by his exact researches to conclude that it "is only an illusion, a pure hypothesis definitely contradicted by experiment." The hypothesis of Prout was also very definitely rejected by Mendeléeff.

Interest in Prout's hypothesis revived as a result of the experiments of Crookes (1887) on the discharge of electricity through highly rarefied gases. As a result of this work, Crookes was led to assume that the electricity is carried in vacuum tubes by a "fourth state of matter," as much more attenuated than ordinary gases as the latter are removed from the liquid state. This fourth state of matter he identified with protyle, and regarded the atoms of the elements as condensations of the primary matter. Later investigations have confirmed these bold speculations in a surprising manner (p. 1035).

Apart from hypothetical considerations, a number of interesting regularities appear from an inspection of the periodic system itself.

The mean difference between the atomic weights of corresponding elements in series 2 and 3 is 16; that in series 3 and series 4 is 18½. The average difference between the atomic weights in series 4 and 6 and 5 and 7 is 46, which persists between series 6 and 8, until the group of rare earth elements is reached, when it

SERIES	GROUP 0.	GROUP I.	GROUP II	GROUP III.	GROUP IV.
	— —	R_2O RH	R_2O_2 RH_2	R_2O_3 —	R_2O_4 RH_4
1		**H 1·000**			
2	He 3·97	Li 6·89	Be 9·00	B 10·8	C 11·910
3	Ne 20·0	Na 22·82	Mg 24·13	Al 26·8	Si 28·1
4	A 39·6	K 38·79	Ca 39·75	Sc 44·7	Ti 47·72
5		Cu 63·07	Zn 64·85	Ga 69·5	Ge 71·9
6	Kr 82·26	Rb 84·77	Sr 86·93	Yt 88·62	Zr 89·9
7		Ag 107·04	Cd 111·51	In 113·9	Sn 117·8
8	Xe 129·2	Cs 131·76	Ba 136·28	La 137·9 (and 12 other elements of RareEarths)	Ce 139·15
9		Au 195·6	Hg 199·0	Tl 202·4 Ra-C_2 Ac-D Th-D	Pb 205·55 Pb *ex* Ra-C_2 Pb *ex* Ra-F Pb *ex* Ac-D Pb *ex* Th-C_1 Pb *ex* Th-D Ra-B Ra-D Ac-B Th-B
10	Nt or Ra-Eman 220·6 Ac-Eman Th-Eman.	—	Ra 224·2 Ac-X Ms Th_1 Th-X	Ac? Ms Th_2	Th 230·31 U-X_1 Io U-Y Rd-Ac Rd-Th

THE ELEMENTS.

GROUP V.	GROUP VI.	GROUP VII	GROUP VIII.		
R_2O_5 RH_3	R_2O_6 RH_2	R_2O_7 RH			
N 13·897	O 15·87	F 18·9			
P 30·79	S 31·81	Cl 35·18			
V 50·6 As 74·37	Cr 51·6 Se 78·6	Mn 54·49 Br 79·29	Fe 55·40	Co 58·50	Ni 58·21
Nb 92·4 Sb 119·2	Mo 95·2 Te 126·5	— I 125·91	Ru 100·9	Rh 102·1	Pd 105·9
Ta 180·1 Bi 206·4 Ra-C_1 Ra-E Ac-C Th-C	W 182·5 Po or Ra-F Ra-A Ra-C Ac-A Th-A Th-C_1	— —	Os 189·4	Ir 191·6	Pt 193·6
Eka Ta U-X_2	U-I 236·3 U-II				

rises to 89. The value falls again to 54 when the rare earths are passed.

Rydberg (1914) observed that the two short periods, from Li to Ne, and from Na to A, contain altogether $2 \times 8 = 4^2$ elements. The two long periods, from K to Kr, and Rb to Xe, contain $2 \times 18 = 6^2$ elements. These should, if the same regularity holds good, be followed by two very long periods containing $2 \times 32 = 8^2$ elements, of which 56 are known from Cs to U. On the other hand, we should expect the two short periods to be preceded by periods containing 2^2 elements, of which helium and hydrogen are known. Helium may be considered as the fourth element; experiments on the scattering of X-rays by gases indicate consecutive positions for hydrogen and helium, so that two hypothetical gases should *precede* hydrogen. Rydberg, however, considers that these elements should come between H and He, and identifies them with coronium and nebulium, evidence of the existence of which has been found in the spectra of nebulæ. Nicholson, on the other hand, from spectroscopic evidence, believes that the upper period contains, besides hydrogen, the hypothetical elements protohydrogen (0·081), nebulium (1·31), protofluorine (or coronium, 2·1), arconium (2·9), etc. The existence of coronium (supposed by Mendeléeff to have an atomic weight 0·4) has been inferred from the bright green lines seen in the spectrum of the sun during the eclipse of 1869; although traces of it were said to exist in volcanic gases by Nasini, Anderlini, and Salvadori (1893), its presence on the earth is doubtful. Mendeléeff also regards the luminiferous ether as an inactive element of atomic weight about 10^{-6}.

Correction of atomic weights.—Mendeléeff found it necessary to alter some atomic weights in use in 1869 in order that the elements should fall into those positions in the periodic table assigned to them by their chemical properties. Thus, **indium**, which occurs with zinc in minerals, has an equivalent of 37·9. From its occurrence with zinc, the element was supposed to be bivalent, the oxide being InO; hence the atomic weight would be $37{\cdot}9 \times 2 = 75{\cdot}8$. The element should then go in Group II after zinc, but this position is occupied by strontium (87), and there is no place for an element of atomic weight 75·4 in that group. There is also no place between As = 75 and Se = 79, so that this atomic weight is impossible. The vapour density, atomic heat, and isomorphism methods had not been applied, so that there was no guidance available. Mendeléeff pointed out that if indium is tervalent, its oxide being In_2O_3, its atomic weight would be $37{\cdot}9 \times 3 = 113{\cdot}7$, when it would fill a vacant space in Group III, between Cd = 112 and Sn = 118, in the preceding and following groups, respectively. The chemical and physical properties agree with this position. Thus, the densities are Cd 8·6, In 7·4, Sn 7·2; the basic properties of In_2O_3 are intermediate between CdO and SnO_2; finally, the specific heat of indium was found to be 0·055, indicating an atomic weight of $6{\cdot}3/0{\cdot}055 = 114{\cdot}5$. The element was then found to form alums, and therefore belongs to Group III.

Again, **beryllium,** with the equivalent 4·55, seemed to show many resemblances to aluminium. The hydroxides of both elements are gelatinous precipitates soluble in acids and alkalies; the carbonates cannot be prepared by precipitation, but decompose immediately; and the metals, obtained by the electrolysis of the double fluorides of aluminium and beryllium with potassium, dissolve in alkalies with liberation of hydrogen. The determination of the specific heat of beryllium, finally, led to the value 13·65 for the atomic weight. All these results appeared to point to beryllium being tervalent, the oxide Be_2O_3 resembling Al_2O_3. But there is no place for an element of this atomic weight in the first period: B 11 C 12 N 14 O 16. Avdéeff (1819) had previously pointed out the analogy of the sulphate with that of magnesium, and Mendeléeff placed beryllium in Group II, before Mg, thus considering it to be bivalent, and its oxide BeO. Its atomic weight should then be $4·55 \times 2 = 9·1$, and there is a vacant place between Li = 7 (univalent) and B = 11 (tervalent) for such a bivalent element. Humpidge then found that the specific heat of beryllium increases rapidly with the temperature, becoming 0·6206 at 500°: this gives Be = 9·8. Nilson and Pettersson (1884) also found that the vapour density of beryllium chloride was 40, which agrees with $BeCl_2$ ($9 + 71 = 80$), but not with $BeCl_3$ ($13·65 + 106·5 = 120·15$). These chemists, therefore, abandoned their advocacy of the tervalent character of beryllium.

In other cases the correction in the atomic weight amounted to a few units only, the valency remaining unaltered.

Thus, **gold** was formerly placed before iridium, platinum, and osmium, in the order given, in the atomic weight sequence (H = 1):

Au 194·6	Ir 195·1	Pt 195·1	Os 197·0

Chemical analogies in the periodic system strongly suggest the order:

Os 189·4	Ir 191·6	Pt 193·6	Au 195·6

and more exact determinations gave the atomic weights shown.

Prediction of missing elements.—It has been mentioned that, in arranging the elements in the periodic system, Mendeléeff had to leave gaps in order that the chemical analogies should be preserved. Thus, the next known element after calcium (Ca = 40) was titanium (Ti = 48). But if titanium were placed after calcium, it would come in the third group, under aluminium, whereas its properties indicate that the element is quadrivalent and ought to go in the fourth group, under silicon:

Be	9	B	11	C	12	N	14
Mg	24	Al	27	Si	28	P	31
Ca	40		—	Ti	48	V	51
Zn	65		—		—	As	75

There was therefore a gap left in the third group, between calcium and titanium. Two similar gaps were also left in the next period. Mendeléeff predicted that these would be filled by unknown elements, which he called **ekaboron, eka-aluminium,** and **ekasilicon,** respectively.

From the regularities of the atomic weights of the known elements he was able to predict the atomic weights of the missing elements, and from the positions in the table, he foreshadowed their properties in some detail. These predictions were brilliantly verified by the discovery of **scandium** (Nilson, 1879), **gallium** (Lecoq de Boisbaudran, 1875), and **germanium** (Winkler, 1886).

In the table below are given the predicted and observed properties of **germanium ;** these show how closely the predictions were followed (Mendeléeff, "Principles of Chemistry," II, 27). It has been said that these predictions could have been made without the Periodic Law ; it may reasonably be asked why this had not in fact been done.

EKASILICON (Es) ; predicted by Mendeléeff, 1871.	GERMANIUM (Ge), discovered by Winkler, 1886.
Atomic weight 72.	Atomic weight 71·9.
Density 5·5.	Density 5·47.
Atomic volume 13.	Atomic volume 13·2.
Colour of element : dirty grey, giving a white powder of EsO_2 on calcination.	Element is a greyish-white metal, giving a white powder, GeO_2, on ignition.
Metal will decompose steam with difficulty.	Metal does not decompose water.
Action of acids will be slight ; that of alkalies more pronounced.	Metal is not attacked by HCl ; it dissolves in *aqua regia* ; aqueous KOH has no action, but molten KOH oxidises Ge with incandescence.
Element will be obtained by action of Na on EsO_2, or K_2EsF_6.	Element obtained by reduction of GeO_2 by carbon, or of K_2GeF_6 by Na.
Oxide EsO_2 will be refractory, and have sp. gr. 4·7. Basic properties of oxide less pronounced than those of TiO_2 or SnO_2, but more marked than those of SiO_2.	Oxide GeO_2 refractory ; sp. gr. 4·703 ; very feebly basic, although indications of oxy-salts are found.

EKASILICON (Es); predicted by Mendeléeff, 1871.	GERMANIUM (Ge), discovered by Winkler, 1886.
Hydroxide soluble in acids, but solutions will readily hydrolyse with deposition of meta-hydroxide.	Acids do not pp. hydroxide from dilute alkaline solutions ; from concentrated solutions, acids or CO_2 pp. GeO_2 or meta-hydroxide.
Chloride $EsCl_4$ will be a liquid, b.-pt. below 100°, sp. gr. 1·9 at 0°.	$GeCl_4$ is a liquid, b.-pt. 96°, sp. gr. 1·887 at 18°.
Fluoride, EsF_4, will not be gaseous.	$GeF_4,3H_2O$ is a white crystalline solid.
Organo-metallic compounds will be formed ; *e.g.*, $Es(C_2H_5)_4$, b.-pt. 160°, sp. gr. 0·96.	$Ge(C_2H_5)_4$, b.-pt. 160°, sp. gr. slightly less than that of water.

The reader should have no difficulty in following the predictions of Mendeléeff from a consideration of the properties of the elements silicon, tin, zinc, and arsenic, which are neighbouring elements in the periodic table. The properties of gallium may also be inferred.

A complete new group, the **zero group,** was added to the table by Ramsay, and numerous gaps in the lowest part of the table have been filled in by the discovery of the radioactive elements (see Chapter LI). The Periodic Law therefore points out the possibility of discovering new elements ; it gives indications as to their properties, and with what known elements they are likely to occur. On the other hand, it shows that the number of possible new elements is limited ; in particular, there are no new elements to be discovered between helium (He = 4) and bromine (Br = 80), except possibly in the transitional group or the zero group, because there is no place for them in the table.

An important result of the periodic classification is the additional confirmation it affords of the present values of the atomic weights, and of the belief in the elementary character of the simple substances.

Difficulties in the periodic system.—The periodic classification, in the form given to it by Mendeléeff, is not free from difficulties and apparent contradictions. One of the most serious is the **inverted positions** of three pairs of elements (A, K ; Co, Ni ; Te, I). Again, it is very difficult to fit in the elements of the **rare earths** (p. 461). The **transitional elements** occupy an exceptional position ; attempts to include them in the other groups have not been successful.

The arrangement into groups overlooks some **chemical analogies,** such as those between boron and carbon, copper and mercury ;

and also brings together elements which have little real analogy, such as manganese and chlorine. The analogies between successive elements in a period, pointed out by Mendeléeff, has, however, often been neglected. Thus, the metals of the horizontal period: V, Cr, Mn, Fe, Co, Ni, are chemically related; and the sulphates, $RSO_4, 7H_2O$, of Mn, Fe, Co, Ni, Cu, Zn, are isomorphous.

The most remarkable difficulty, however, is the **position of hydrogen** in the system. It is usually omitted altogether, but may be given a whole period above the first complete period beginning with helium. If it is placed in this period in Group I with the alkali-metals, to which it shows resemblance in its electropositive character and in forming an alloy with palladium, there must be a number of other unknown elements in the period with atomic weights between 1 and 4. The only other group in which a univalent element could be placed is the halogen group, Group VII. But, although hydrogen is a non-metal, can be replaced atom for atom by halogens in organic compounds, and is a gas more difficult to liquefy than fluorine, yet the period should then contain unknown elements with atomic weights less than 1 (p. 468). However placed, hydrogen occupies an exceptional position: its best situation is probably at the head of Group I, on account of its electropositive character, although some recent physical experiments place it with the halogens.

EXERCISES ON CHAPTER XXIV

1. What steps would you take to ascertain (*a*) the atomic weight, (*b*) the position in the periodic system, of a newly discovered metal?

2. Discuss the positions of (*a*) hydrogen, (*b*) potassium, (*c*) manganese, (*d*) cobalt in the periodic system.

3. On what grounds was Mendeléeff able to predict the existence and properties of gallium, scandium, and germanium?

4. Discuss the reasons, other than the values of the atomic weights, which justify the following pairs of elements being placed in the same groups: beryllium and zinc; iron and platinum; sodium and copper; sulphur and chromium. With what other elements of other groups do you consider each of these elements to be chemically related?

5. Give a brief account of Prout's hypothesis. What bearing has it on the interpretation of atomic weights?

6. Discuss the position of iodine and tellurium in the periodic system. What similar cases are known?

7. What position is assigned to the rare-earth elements in the periodic table? What other alternative methods of classification would be possible?

CHAPTER XXV

SULPHUR AND ITS COMPOUNDS WITH HYDROGEN AND HALOGENS

Sulphur.—From its occurrence in the free state in Sicily, in the centre of Roman civilisation, **sulphur**, or **brimstone** (German *Brennstein, i.e.,* combustible stone), has been known from antiquity. The use of sulphur in medicine, and of the fumes of burning sulphur in fumigation, are mentioned by Homer (*c.* 900 B.C.) ; the bleaching of textile fabrics by the fumes was carried out at an early date. The alchemists regarded sulphur as the *principle of combustibility* and a constituent of metals (p. 29). The phlogistonists considered it to be a compound of phlogiston and sulphuric acid ; the former being evolved on burning, and appearing as a flame, whilst the acid was left. Lavoisier (1777) pointed out that it should be regarded as an element, and although Davy (1809) found that ordinary sulphur always contains a little hydrogen, this was recognised as an impurity.

Sulphur **occurs** in Nature either free or in combination. **Free sulphur** occurs in large quantities in Italy, in the volcanic regions of Sicily, and in America, in the southern State of Louisiana. Less important worked deposits occur in New Zealand in Whale Island, in Texas, Chile, Russia, Iceland, and especially in Japan.

In 1884, 447,000 tons of sulphur were exported from Sicily, and 41,000 tons from the rest of the world. In 1913, Louisiana and Texas alone produced 250,000 tons; Sicily 407,307 tons, Japan 58,452 tons, and new Zealand (in 1914) 12,000 tons. More than 800,000 tons are now said to be produced per annum in Louisiana.

Sicilian sulphur occurs stratified with marl, clay, and rock, mostly gypsum, $CaSO_4,2H_2O$, limestone, and quartz. It is found occasionally in large, yellow, transparent crystals (Fig. 257), but usually in crystalline masses, which are yellow or grey in colour. Since fused sulphur deposits monoclinic crystals, which crumble on standing to very small rhombic crystals, the origin of the deposits, which contain large crystals, can hardly be igneous, although rhombic crystals may have been deposited on very slow cooling. The sulphur in the craters of extinct volcanoes is formed by the interaction of **volcanic gases,** containing hydrogen sulphide and sulphur dioxide: $2H_2S + SO_2 = 2H_2O + 3S$, probably derived from pyrites. Since gypsum and calcium carbonate are always found with the beds of sulphur, the latter are assumed to be the result of the reduction of **gypsum** by organic matter and bacteria: $2CaSO_4 + 3C = 2CaCO_3 + 2S + CO_2$.

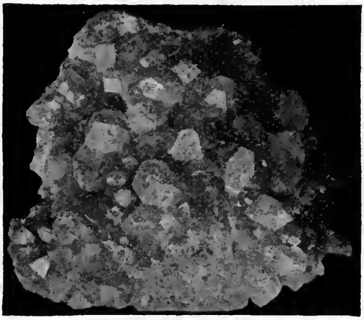


FIG. 257.—Native Sulphur (British Museum).

EXPT. 173.—Invert a jar of sulphur dioxide over one of sulphuretted hydrogen. No action occurs. Add a little water and shake. The water becomes turbid, from separation of sulphur, but no action occurs in the gases. The latter must therefore react in solution: $2H_2S + SO_2 = 2H_2O + 3S$.

Combined sulphur occurs in the form of **metallic sulphides**, many of which are important **ores** of metals (*i.e.*, serving for their extraction). *E.g.*, lead sulphide, or *galena*, PbS; zinc sulphide, or *blende*, ZnS; *copper pyrites*, Cu_2S,Fe_2S_3; and *iron pyrites*, FeS_2 (used as a source of sulphuric acid). **Hydrogen sulphide**, H_2S, occurs in volcanic gases, and in some mineral springs, often with gaseous **carbon oxysulphide,** COS. **Sulphur dioxide,** SO_2, also occurs in volcanic gases. Some springs and rivers (Rio Canea and Rio Vinagre, in America) contain free **sulphuric acid**, H_2SO_4. Large masses of *gypsum*, or calcium sulphate, $CaSO_4,2H_2O$, and other **metallic sulphates,** are common. Sulphur is a constituent of some kinds of organic matter; thus the blackening of silver spoons by eggs is due to the sulphur contained in the albumin of the latter. It is found in certain bacteria, *e.g.*, *Beggiatoa alba*, which are capable of decomposing sulphur compounds in their life-processes. The pungent principles of onions, garlic, horse-radish, and mustard are organic sulphur compounds. Combined sulphur is present in hair and wool, and in most animal and vegetable matter.

EXPT. 174.—Fuse a little hair with caustic soda in a test-tube. Dissolve the cool mass in water, and pour on a silver coin. The latter is at once turned black, through formation of silver sulphide, Ag_2S.

The manufacture of sulphur.—Native sulphur, as it is dug in Sicily, contains 15–25 per cent. of sulphur. It is stacked in lumps in brick kilns, called *calcaroni*, built on sloping hillsides, with air-spaces, and covered with powdered ore (Fig. 258). The ore is kindled at the bottom, and the heat of combustion of about 30 per cent. of the sulphur serves to melt the rest, which flows off into wooden moulds. The blocks so formed still contain 3–5 per cent. of the original rock, and are exported to Marseilles for purification, since fuel is too dear in Italy.

Improved methods of extraction are being introduced, *e.g.*, the use of the **Gill kiln** (1880), in which the heating is performed in closed brick chambers, with six compartments in a circle, in the interior of which a coke fire is kept burning. About 75 per cent. of the sulphur is recovered. Payen and Gill (1867) also proposed to melt out the sulphur with superheated steam; the apparatus devised for this purpose by Thomas (1869) is in use to a limited extent in the Romagna.

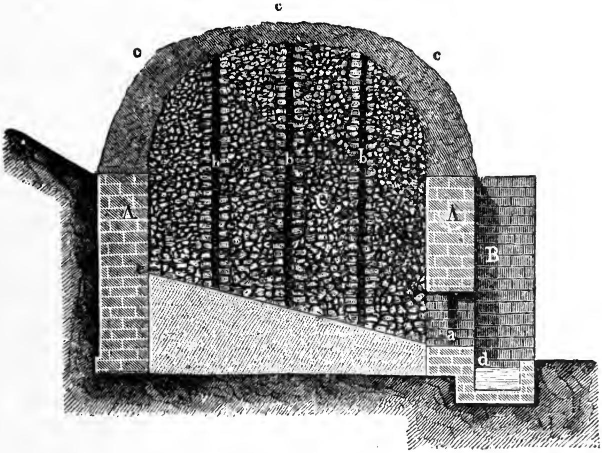


FIG. 258.—Calcaroni, or Sulphur Kiln

Sicilian sulphur is mostly **refined** at Marseilles, with the apparatus shown in Fig. 259. The sulphur is fused in the iron pot, *M*, whence it flows into the iron retort, *G*, heated over a fire. The sulphur boils, and the vapour is conducted into a large brickwork chamber, *A*. At first the vapour condenses on the cold walls as a light yellow crystalline powder, called **flowers of sulphur**. As the walls become hot, this melts (unless it is removed for sale), and runs down as a liquid to the bottom, whence it is tapped off through *O* into cylindrical moulds, to form **roll sulphur**, or **brimstone**. Such an apparatus produces about two tons of refined sulphur per twenty-four hours. Refining is also carried on at Romagna and Catania.

The **Louisiana process of extraction** is different. The deposit, estimated at 40,000,000 tons, occurs below 900 ft. of clay, quicksand, and rock. A boring is made to the deposit, and four concentric pipes are sunk. Down the two outer pipes superheated water

(155°) is pumped. This fuses the sulphur. Air is then forced down the inner pipe, when an emulsion of water, molten sulphur, and air-bubbles rises to the surface through the remaining annular space. This passes to large wooden vats, where the sulphur, of 99·5 per cent. purity, solidifies, and is ready for immediate use.

Sulphur was formerly prepared by distilling iron pyrites in clay retorts: $3FeS_2 = Fe_3S_4 + 2S$ (*cf.* $3MnO_2 = Mn_3O_4 + O_2$); or by roasting pyrites in kilns with a limited supply of air: $3FeS_2 + 5O_2 = Fe_3O_4 + 3SO_2 + 3S$. It is more economical to burn the pyrites to sulphur dioxide: $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$, and use this as a source of sulphuric acid (p. 503). Sulphur is formed by heating metallic sulphides to 1000° in carbon dioxide: $FeS + CO_2 = FeO + CO + S$.

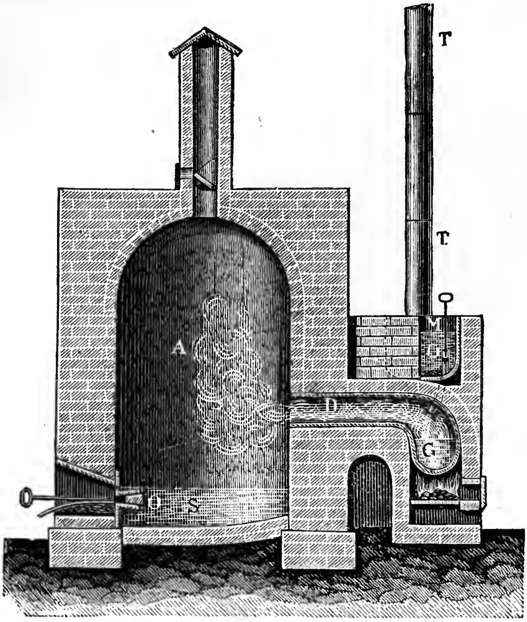


FIG. 259.—Refining of Sulphur by Distillation.

Sulphur from alkali-waste.—Some sulphur is extracted from Leblanc **alkali-waste** (containing insoluble **calcium sulphide**, CaS), by the **Chance-Claus process.** A suspension of the waste in water is treated with limekiln gas, containing carbon dioxide, in large iron vessels called *carbonators.* Sulphuretted hydrogen is evolved: (1) $CaS + CO_2 + H_2O = CaCO_3 + H_2S$. The gas, however, is too largely diluted with nitrogen (present in the kiln gas) to pay for treatment. It is therefore passed into a second carbonator where the sulphuretted hydrogen is absorbed, the insoluble CaS passing into solution as **calcium hydrosulphide,** $Ca(HS)_2$: (2) $CaS + H_2S = Ca(HS)_2$. When all the CaS in the first vessel is decomposed, this is cleaned out and filled with fresh waste, and the connections are changed so that the kiln gas passes directly into the second vessel. The

$Ca(HS)_2$ is then decomposed: (3) $Ca(HS)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S$. The gas leaving the carbonator now contains, for a given volume of nitrogen in the kiln gas passing through, *twice* as much H_2S as that from CaS in the first vessel, since equal volumes of CO_2 are taken up in reactions (1) and (3). It is collected in a large gas-holder over water covered with a layer of oil. This gas is then mixed with air, and passed over porous oxide of iron on a grating in the **Claus kiln**—a brickwork chamber, with large brick condensing chambers and flues beyond. The oxide is heated to start the reaction, which then proceeds automatically: (4) $2H_2S + O_2 = 2H_2O + 2S$. The oxide of iron is unchanged, and acts as a *catalyst.* Probably part of the H_2S burns to SO_2, which decomposes the rest: $2H_2S + SO_2 = 2H_2O + 3S$—both SO_2 and H_2S are found in the waste gases after the sulphur has condensed in the chambers: 35,000 tons of sulphur are recovered in England annually by this process.

Sulphur from spent oxide.—Sulphur may also be extracted from the **spent oxide** of the gasworks. Coal contains pyrites, FeS_2, the sulphur of which, during distillation in the manufacture of gas, comes off chiefly as sulphuretted hydrogen, H_2S, and carbon disulphide, CS_2 The former is removed by passing the crude gas over hydrated oxide of iron, $Fe(OH)_3$, mixed with sawdust, in purifiers: $2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O$. When the mass is no longer active, it is "revived" by exposure to air: $2Fe_2S_3 + 3O_2 + 6H_2O = 4Fe(OH)_3 + 6S$. After these operations have been repeated several times, the "spent oxide" contains about 50 per cent. of free sulphur. It is then usually burnt in a current of air to produce sulphur dioxide (p. 503). The sulphur may be extracted from the material by solution in carbon disulphide, but some tarry matter also dissolves.

Uses of sulphur.—**Crude sulphur** is used for making sulphur dioxide (and thence sulphuric acid), and in the manufacture of carbon disulphide (p. 710). **Refined sulphur** is used in medicine, in the form of powder as a fungicide, and in the preparation of gunpowder, matches, fireworks, and dyes. Sulphur is also used in large quantities for *vulcanising* rubber.

Rubber, or caoutchouc, is a natural hydrocarbon obtained from the juices of several tropical trees. In the untreated state, the elasticity slowly disappears on warming and cooling, and to prevent this the rubber is **vulcanised** (Hancock and Brockedon, 1847) by heating with 10–12 parts of sulphur at 140°, or by treating with a solution of sulphur in sulphur chloride (p. 488). With larger quantities of sulphur (25–40 per cent.) a hard mass of **vulcanite,** or **ebonite,** is formed.

For use in dressing vines (to prevent the growth of the fungus *oidium*), sulphur is finely ground between millstones, and sieved through silk

(170 meshes to the inch). By blowing a current of air through the mill, the very finest particles ("winnowed sulphur") are carried off, and are retained by cloth filters.

The allotropic forms of sulphur.—Sulphur exists in two common **crystalline forms** : (1) **rhombic**, or **α-sulphur** (Fig. 260), and (2) **monoclinic**, or **β-sulphur** (Fig. 261). It also exists in different **amorphous forms,** *e.g.*, **plastic sulphur,** or **γ-sulphur** (now called μ-sulphur), and **colloidal sulphur.**

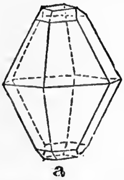


FIG. 260.—Crystals of Rhombic Sulphur.

Native sulphur occurs in about thirty-six crystalline varieties, all belonging to the rhombic system (p. 438). **Rhombic** or **α-sulphur** is prepared by allowing a solution of sulphur in carbon disulphide slowly to evaporate (p. 10), when pale-yellow, transparent crystals are formed, giving a lemon-yellow powder. The density of α-sulphur is 2·06, and its melting point is 112·8°. It is insoluble in water, very slightly soluble in alcohol and ether, freely soluble in carbon disulphide, sulphur chloride (S_2Cl_2), and hot benzene and turpentine. Rhombic sulphur is *the stable form at the ordinary temperature,* and *all the other forms pass into α-sulphur on standing.* Roll sulphur consists almost entirely of rhombic sulphur ; flowers of sulphur are principally composed of it (70 per cent.), but contain also a white amorphous variety insoluble in carbon disulphide.

Monoclinic or **β-sulphur** was discovered in 1823 by Mitscherlich. Sulphur is **dimorphous,** *i.e.*, it exists in two distinct *crystalline* forms. β-sulphur is produced when fused sulphur is allowed to crystallise.

EXPT. 175.—Half fill a beaker with small pieces of roll sulphur, and heat gently on a sand-bath till the whole is just fused. Allow to cool until a crust forms on the surface. Make two holes in this crust (one to admit air) with a pointed glass rod, and pour the still liquid portion into a dry porcelain dish. The inside of the beaker will be found to be lined with beautiful, interlacing, transparent, flexible, needle-shaped crystals (Fig. 261) of **β-sulphur,** having a deeper yellow colour than α-sulphur. On standing for a few days, the crystals become opaque and brittle, and the colour becomes lemon-yellow. The crystals now consist of aggregates of minute crystals of α-sulphur, although the original monoclinic form is preserved by the whole crystal, which is therefore called a **pseudomorph.** The gradual

FIG. 261.—Crystal of Monoclinic Sulphur.

transition from one form to the other is readily followed by the colour.

β-Sulphur, when quickly heated, melts at 119·25°, and has a density of 1·96. It is insoluble in water, but soluble in carbon disulphide; the solution on evaporation deposits α-sulphur.

Two other varieties of β-sulphur, with slightly different angles, are produced (i) by cooling in a freezing mixture a solution prepared by heating sulphur with benzene, toluene, alcohol, or carbon disulphide in a sealed tube; (ii) by allowing an alcoholic solution of sodium sulphide, saturated with sulphur, to stand in the air, when oxidation occurs, and crystals grow on the surface. The crystals formed by process (i) are thin flakes, called **nacreous sulphur** (French, *nacre*, mother-of-pearl). Those formed in process (ii) contain hexagonal plates (**tabular sulphur**). Rhombohedral and triclinic forms have also been described.

The transition point of α- and β-sulphur.—Crystals of β-sulphur, as seen in Expt. 175, slowly change at the ordinary temperature into minute crystals of α-sulphur, and become opaque. Crystals of α-sulphur, on the other hand, slowly become opaque if heated above 96°, especially at 110°, and pass into aggregates of minute crystals of β-sulphur. The transformation of S_β into S_α is reversible; below 96°, S_α is the stable form; above 96°, S_β is stable. This temperature, 96°, is called the **transition temperature** or **transition point** of sulphur. At the transition temperature, both crystalline forms are in equilibrium, $S_\alpha \rightleftharpoons S_\beta$.

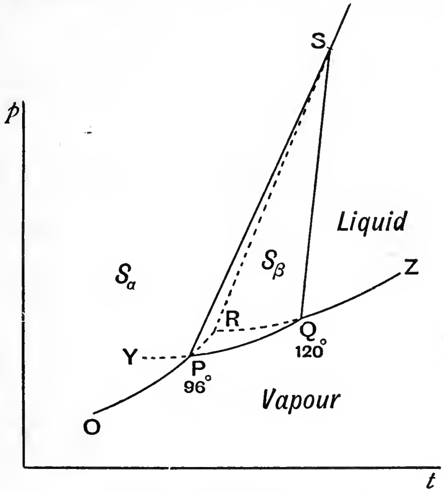


FIG. 262.—Phase Rule Diagram for Sulphur.

Substances, such as sulphur, which exist in two forms, one of which is stable below a certain temperature and the other stable above it, are called **enantiotropic**; substances like iodine chloride, which exist only in *one* stable form, the other forms being unstable in all circumstances, are called **monotropic** (Greek *mono*, one; *enantios*, opposite; *tropos*, form).

Equilibrium between α- and β-sulphur.—α-Sulphur, β-sulphur, liquid sulphur, and sulphur vapour are different **phases** of sulphur (p. 7), and according to the Phase Rule (p. 106) they ought to coexist under certain conditions of temperature and pressure. In Fig. 262, *OP* is the vapour-pressure curve of S_α, *i.e.*, it represents the pressures of sulphur vapour in equilibrium with solid S_α at various temperatures. *QZ* is the vapour-pressure curve of liquid sulphur. The point *R*, which is the point of intersection of *OP* and *QZ*, defines a temperature and pressure at which S_α, liquid S, and S-vapour coexist in equilibrium. It is the melting point of S_α under its own vapour pressure, about 113°, and is a **triple point** (3 phases: S_α, liquid, vapour, in equilibrium, *cf.* p. 92). *PQ* is the vapour-pressure curve of β-sulphur, meeting *QZ* at *Q*. *Q* therefore defines the temperature and pressure at which S_β, liquid S, and S-vapour are in equilibrium—it is another triple point, viz., the melting point of β-sulphur under its own vapour pressure, 120°.

PQ also crosses *OP* at *P*. *P* is the triple point at which S_α, S_β, and S-vapour coexist; it is the **transition point** of α- and β-sulphur, 96°. Below 96°, α is stable and β unstable; above 96°, β is stable and α unstable. But S_β may exist in a **metastable** condition below 96°, because the change $S_\beta \rightarrow S_\alpha$ takes place only slowly. The prolongation of *QP* to *Y* expresses this fact, *PY* being the vapour-pressure curve of S_β at temperatures below 96°. The melting points of α- and β-sulphur are raised by pressure (*cf.* ice, p. 91), but at different rates. This is represented by two lines, starting from *P* and *Q* with different slopes ($\delta T/\delta p$), and meeting ultimately at *S* (151°; 1228 atm.), where S_α, S_β, and liquid S are in equilibrium. Above this point S_β cannot exist, and the region of existence of S_β is confined to the area *PSQ*. The areas defining the regions of existence of S_α, liquid, and vapour are marked. The point *R* is inside the region of S_β, hence the melting point of S_α is a metastable point; it can be realised only because the change $S_\alpha \rightarrow S_\beta$ is so slow that fusion of the former, at its appropriate melting point (112·8°), takes place before the change $S_\alpha \rightarrow S_\beta$, which begins at 96°, has proceeded appreciably. If S_α is kept at a temperature below 112·8° but above 96° for a long time, and then heated, it will not melt at 112·8°, but at 120°, since it is now all converted into S_β.

Amorphous sulphur.—Expt. 176.—If pieces of roll sulphur are heated in a flask they melt to a clear yellow liquid at 112·8°. This is called S_λ. On cooling rapidly in water, S_α is produced, completely soluble in CS_2. If the temperature is now gradually raised, the liquid, at first quite mobile, suddenly becomes very viscous, and its colour darker yellow at 180–190°. At 230° the liquid is black and viscous. This form of the liquid is called S_μ. Beyond 230° the viscosity decreases, but the colour remains dark, and the sulphur finally boils at 444°.

If the boiling liquid is poured into cold water it forms soft, sticky, rubber-like, transparent threads, called **plastic sulphur, γ-sulphur,** or **μ-sulphur.**

S_μ has a density of 1·96; it is insoluble in carbon disulphide. On standing for a few days the threads form an opaque, brittle solid, lemon-yellow in colour, consisting mainly of S_α. About 34 per cent. of the solid is still insoluble in carbon disulphide, and consists of S_μ. At 100°, the change from viscous liquid to solid takes place in an hour.

It has been found that the darkening in colour is due to organic impurities, and that S_μ (plastic sulphur) is only formed if slightly impure sulphur, which has been exposed to air and contains sulphuric acid, is used. If ammonia gas is passed through the melted sulphur, no plastic sulphur is formed on further heating. In the liquid, S_λ and S_μ exist in equilibrium at various temperatures: $S_\lambda \rightleftharpoons S_\mu$. *E.g.*, the percentages of S_μ are: at 120°, 3·6; 160°, 11; 444·7°, 30. A trace of iodine stabilises S_μ.

Two other varieties of sulphur have recently been described. S_π is obtained when sulphur is heated above the melting point and rapidly cooled; its solution in carbon disulphide has a deep yellow colour. S_ϕ is produced when concentrated hydrochloric acid at 0° is added to a cold solution of sodium thiosulphate and the mixture shaken with toluene. After a short time orange-yellow crystals of S_ϕ separate from the toluene, having a distinct form and solubility. The solutions of S_ϕ are yellow, but not so strongly as those of S_π.

If 2 parts of flowers of sulphur are boiled with 13 parts of water and 1 part of lime slaked with 3 parts of water, the clear liquid decanted is deep reddish-yellow in colour, and contains polysulphides of calcium, $CaS{\cdot}S_n$, *e.g.*, CaS_5. The early Greek alchemist Zosimus refers to this liquid as "the divine water" (*thion hudor*), or "the bile of the serpent." Pliny stated that it was used by the Romans to give a dark gloss to silver—"oxidised" silver is so made to-day. The Latin Geber stated that if an acid be added to the liquid, a very offensive smell (sulphuretted hydrogen) is noticed, and a fine *white* precipitate of sulphur is formed. This is called **milk of sulphur** (*lac sulphuris*), and is prepared for pharmaceutical purposes. It is soluble in carbon disulphide.

If the *thion hudor* is precipitated with dilute sulphuric acid, the resulting sulphur may contain calcium sulphate; this is left as a residue on burning a little of the sulphur on platinum foil.

Another amorphous variety of sulphur remains as a pale yellow powder when "flowers of sulphur" are treated with carbon disulphide. This form also separates when a solution of sulphur in carbon disulphide is exposed to sunlight, or on the decomposition of sulphur chloride by water.

Colloidal sulphur is formed in the preparation of milk of sulphur: the filtered liquid is a turbid emulsion of minute drops of *liquid* sulphur soluble in CS_2, and doubly-refracting (**liquid crystals**). If a solution of sodium thiosulphate ("hypo") is acidified, it quickly forms a turbid colloidal suspension of minute *solid* crystals of sulphur, insoluble in CS_2. If the milky liquid obtained by passing sulphuretted hydrogen into a solution of sulphur dioxide is evaporated, a gum-like residue is left, part of which is soluble and part insoluble in CS_2. These varieties of colloidal sulphur were called **δ-sulphur** by Debus (1888).

Sulphur vapour.—Sulphur boils at 444·7°, and forms a deep red **vapour,** which, when strongly heated, becomes yellow. Dumas (1832) found the vapour density at 524° to be 96, which corresponds with the molecule S_6; at higher temperatures the density fell, and Dumas thought the molecules S_4 and S_2 were formed. Biltz (1901), working with a wider range of temperatures, found the following densities: 468°: 113 (higher than S_7); 524°: 102 (higher than Dumas' figure); red heat: 32·2 (S_2). He concluded that at lower temperatures the molecule is S_8, but this is partially dissociated even at the boiling point. There was no evidence of a constant density over any range of temperature, and Biltz considered that the molecule S_8 broke up at once into S_2: $S_8 \rightleftharpoons 4S_2$. The lowering of vapour pressures of CS_2 and S_2Cl_2 containing dissolved sulphur gives the formula S_8 for the latter. Bleier and Kohn (1900) found that the vapour density rises when the boiling point is lowered by diminished pressure. At 214° (2 mm. pressure) the density corresponds with $7\frac{1}{2}$ atoms in the molecule. Preuner (1903) considers that S_6 and S_4 also occur in the vapour: $S_8 \rightleftharpoons S_6 + S_2 \rightleftharpoons S_4 + 2S_2 \rightleftharpoons 4S_2$. Nernst found that 45 per cent. of the S_2 molecules were broken up into atoms at 1900–2000°: $S_2 \rightleftharpoons 2S$.

Pure sulphur.—H. B. Baker purified sulphur by heating the vapour with S_2Cl_2 at 450°, when the hydrogen present as impurity forms H_2S, which reacts with S_2Cl_2 to form HCl and S. The S_2Cl_2 and HCl were removed by heating *in vacuo*, and the sulphur left was so pure that it could be distilled unchanged in oxygen dried over phosphorus pentoxide (*cf.* p. 704).

Compounds of sulphur with hydrogen.—Sulphur forms a gaseous compound H_2S, **hydrogen sulphide**, or **sulphuretted hydrogen,** analogous to water, H_2O. In a series of analogous compounds of related elements, the boiling point rises with the atomic weight of the element; hence Vernon infers that water, which should boil at a lower temperature than H_2S, must be associated, $(H_2O)_n$ (*cf.*

p. 201). Two liquid **hydrogen persulphides,** H_2S_2, H_2S_3, are known (*cf.* H_2O_2).

Sulphuretted hydrogen, H_2S.—When hydrogen is passed over boiling sulphur in a bulb-tube, the issuing gas contains a small amount of sulphuretted hydrogen (1–2 per cent.), and blackens lead acetate paper, owing to the formation of lead sulphide, PbS (Expt. 177). If pure sulphuretted hydrogen is heated, partial decomposition occurs, with deposition of sulphur. The reaction is therefore reversible : $H_2 + S \rightleftharpoons H_2S$, and a state of equilibrium is reached. At 310°, the combination $H_2 + S = H_2S$ is almost complete after a week, whilst if a stream of powerful sparks is passed through H_2S, sulphur is deposited, and the gas left, which occupies the same volume, is nearly pure hydrogen.

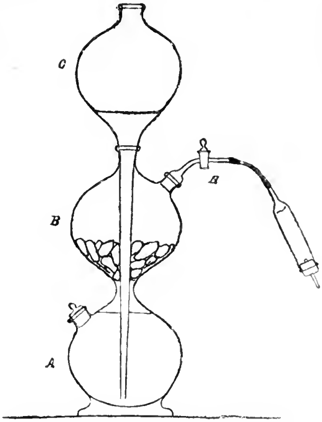


Fig. 263.—Kipp's Apparatus for H_2S.

Traces of sulphuretted hydrogen are formed when sulphur is boiled with water : $2H_2O + 2S \rightleftharpoons 2H_2S + O_2$. The gas is also formed when heavy naphtha (sp. gr. 0·9) is dropped into boiling sulphur in a flask ; part of the hydrogen in the hydrocarbon is **substituted** by sulphur (S replaces 2H), and forms H_2S (*cf.* p. 398).

Sulphuretted hydrogen is usually prepared by the action of dilute sulphuric, or hydrochloric, acid on **ferrous sulphide :** $FeS + H_2SO_4 = FeSO_4 + H_2S$. The reaction is carried out in a Kipp's apparatus (Fig. 263), so that the supply of the gas, which has a most unpleasant odour and is a blood-poison, may be interrupted at will. On account of the invariable presence of free iron in the ferrous sulphide, the gas so prepared contains hydrogen, which does not interfere with its use in qualitative analysis.

Hydrogen sulphide free from hydrogen is obtained by boiling powdered native antimony sulphide (*stibnite*) with concentrated hydrochloric acid : $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$. The pure gas is also formed by treating calcium or magnesium sulphides with acid : $CaS + 2HCl = CaCl_2 + H_2S$; or by heating to 60° a solution of magnesium hydrosulphide, obtained by passing the impure gas from FeS through magnesia suspended in water :

$$MgO + 2H_2S \rightleftharpoons Mg(HS)_2 + H_2O.$$

This is a reaction of **hydrolysis** (p. 360).

When *concentrated* sulphuric acid is heated with zinc, sulphuretted hydrogen is formed : $4Zn + 5H_2SO_4 = 4ZnSO_4 + 4H_2O + H_2S$.

The action of acids on sulphides.—Ferrous sulphide is very slightly soluble in water, and is almost wholly ionised at the great dilution : (1) $FeS \rightleftarrows Fe^{\cdot\cdot} + S''$. The solubilities of some sparingly soluble sulphides are given below, in gm. mols. per litre :

MnS	$2{\cdot}6 \times 10^{-8}$	PbS	2×10^{-14}	Ag_2S	2×10^{-17}
FeS	6×10^{-10}	CdS	7×10^{-15}	CuS	10^{-21}
ZnS	7×10^{-12}	Bi_2S_3	3×10^{-19}	HgS	3×10^{-27}(?)

Sulphuretted hydrogen is a weak dibasic acid : (2) $H_2S \rightleftarrows H^{\cdot} + HS' \rightleftarrows 2H^{\cdot} + S''$, and the second stage of its ionisation, to S'', is very slight. The concentration of S'' formed in (2) is therefore still less than that formed in consequence of (1), and on adding a strong acid the $H^{\cdot}$ ions of the latter combine with the S'' ions of the sulphide to form H_2S until the concentration $[S'']$ in the solution is reduced to a value compatible with (2). The solubility product of H_2S is then exceeded, the *gas* is formed, and escapes from the liquid. From the equation : $[S''] \times [H^{\cdot}]^2 = \text{const.}$, we see that, since $[S'']$ from the trace of dissolved sulphide is very small, $[H^{\cdot}]$ must be large in order to produce the value of the product corresponding with a saturated solution of H_2S. If the sulphide is *very* sparingly soluble (*e.g.*, CuS, HgS), the necessary concentration of $[H^{\cdot}]$ cannot be produced, even by strong acids, and these sulphides do not dissolve in the latter. When treated with nitric acid (which causes oxidation, with separation of sulphur, or forms sulphuric acid) they dissolve. In the case of cadmium sulphide, CdS, the H_2S accumulating stops the reaction before solution is complete, and very strong acid must be used, or the H_2S must be removed from the liquid by boiling, or by a current of air.

Properties of sulphuretted hydrogen.—The gas may be collected over hot water ; it is appreciably soluble in cold water (4·37 vols. at 0°, 3·58 vols. at 10°, 2·9 vols. at 20° ; 1 vol. of alcohol at 15° dissolves 8 vols. of H_2S). It may also be collected by displacement, since its density is 1·2 (air = 1). It attacks mercury slowly.

Hydrogen sulphide is a colourless gas with a powerful odour of rotten eggs (decaying albumin evolves H_2S), and is poisonous ; it liquefies at − 61·8°, the vapour pressure at 12° being 15 atm. At lower temperatures it forms a transparent solid, melting at − 83°. The critical temperature of H_2S is 100°, the critical pressure 90 atm.

The aqueous solution is **a feeble acid ;** the gas is completely expelled by boiling, and on standing in the air the solution becomes turbid, owing to oxidation and deposition of sulphur : $2H_2S + O_2 = 2H_2O + 2S$. This is retarded by the addition of glycerin (*cf.* p. 494). In decinormal solution 0·07 per cent. is ionised to $H^{\cdot} + HS'$; the further stage, to S'', proceeds only very slightly: $H_2S \rightleftharpoons H^{\cdot} + HS' \rightleftharpoons 2H^{\cdot} + S''$.

The gas is decomposed by sparks, or by a heated platinum spiral: $H_2S \rightleftharpoons H_2 + S$. It is also decomposed by heated sodium, tin, or lead, giving its own volume of hydrogen, and sulphides of the metals: $H_2S + Sn = H_2 + SnS$. Its density is 17, ∴ mol. wt. = 34. Of this, the hydrogen H_2 accounts for 2, ∴ wt. of S = 32, which is the atomic weight; hence the formula of sulphuretted hydrogen is H_2S.

If a jar of chlorine is inverted over one of sulphuretted hydrogen, and the plates are removed, the gas deposits sulphur: $H_2S + Cl_2 = 2HCl + S$ (EXPT. 178). If a solution of sulphuretted hydrogen is treated with a large excess of chlorine water, the solution contains sulphuric acid: $S + 4H_2O + 3Cl_2 = H_2SO_4 + 6HCl$. Hydrogen sulphide, on account of the ease with which it is oxidised, is a **reducing agent**, and is used for this purpose, in aqueous or alcoholic solution.

The gas burns in air or oxygen with a blue flame, and owing to the high temperature it is completely dissociated in the interior of the flame; the latter deposits sulphur on a cold porcelain dish. If the gas in a glass cylinder is ignited at the mouth, a deposit of sulphur is formed on the inside of the jar, owing to the deficiency of oxygen: $2H_2S + O_2 = 2H_2O + 2S$ (EXPT. 179). With a plentiful supply of oxygen, sulphur dioxide is formed: $2H_2S + 3O_2 = 2H_2O + 2SO_2$. A mixture of 2 vols. of H_2S and 3 vols of O_2 explodes violently on ignition.

The gas, or its solution (*e.g.*, mineral waters), may be detected by the black coloration, due to lead sulphide, PbS, produced with lead acetate. If **alkali sulphides** are present, they give a purple colour with a freshly-prepared solution of sodium nitroprusside; this is not produced by free H_2S. The gas decomposes sulphuric acid and calcium chloride, and must be dried over phosphorus pentoxide: $H_2SO_4 + H_2S = S + SO_2 + 2H_2O$. It is absorbed by caustic soda.

Precipitation of metallic sulphides.—Sulphuretted hydrogen precipitates **sulphides** of metals from many solutions of salts of the latter. These sulphides often have characteristic colours, and H_2S is used as a **reagent** in qualitative analysis.

EXPT. 180.—Pass a current of sulphuretted hydrogen through a series of wash-bottles (Fig. 264) containing solutions of lead acetate; copper sulphate; mercuric chloride; arsenious oxide in dilute hydrochloric acid; antimony chloride; cadmium sulphate (*a*) slightly acidified (*b*) strongly acidified, with HCl; notice the effects produced.

Many sulphides are precipitated from solutions acidified with hydrochloric acid: copper, lead, mercuric and bismuth salts, all give

black sulphides; cadmium and arsenic give **yellow** sulphides, CdS, As_2S_3; antimony gives an **orange-red** sulphide, Sb_2S_3; tin (stannous) a **brown** sulphide, SnS.

In some cases metals are precipitated only in *alkaline* solutions. An alkali sulphide, *e.g.*, ammonium sulphide, may be used.

EXPT. 181.—Add ammonium chloride and excess of ammonia to solutions of zinc sulphate, manganous sulphate, and nickel sulphate in bottles, and pass a stream of H_2S through the liquids. Note the colours of the precipitates (ZnS, MnS, NiS).

The **precipitation of sulphides** of metals may be considered from the same point of view as their solution in acids. (i) If the sulphides are very sparingly soluble (PbS, CuS, HgS, As_2S_3, Sb_2S_3, etc.) the concentration of S'' ions formed from them is never large enough, even with relatively high concentrations of $H^{\cdot}$ ions, to give an ionic product $[H^{\cdot}]^2 \times [S'']$ exceeding the solubility product of H_2S, so that the latter cannot be formed. In other words, the sulphides are precipitated even in the presence of acids. (ii) Cadmium sulphide, CdS, occupies an intermediate position. If the acid concentration is greater than $0{\cdot}3\,N$ it is not precipitated. (iii) Sulphides of other metals (FeS, ZnS, MnS) are precipitated in alkaline solution, because then no $H^{\cdot}$ ions are formed:

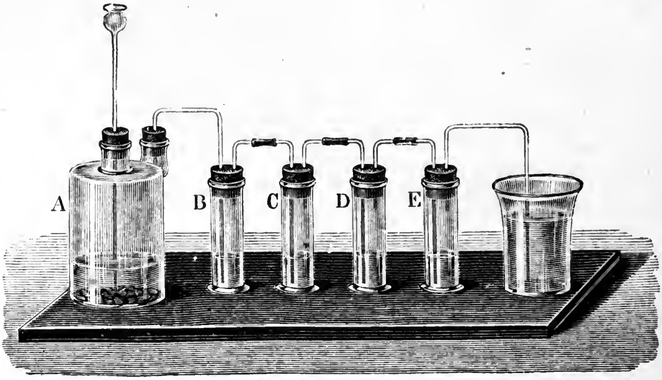


FIG. 264.—Precipitation of Sulphides of Metals.

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

(iv) The metals of the alkalies and alkaline earths are not precipitated, because their sulphides are soluble in water (Na_2S, K_2S), or in a solution of sulphuretted hydrogen ($CaS + H_2S \rightleftharpoons Ca(SH)_2$). (v) Aluminium and chromium salts give precipitates of *hydroxides* with ammonium sulphide, since their sulphides are completely hydrolysed by water:

$$2AlCl_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 6NH_4Cl + 3H_2S \text{ ; or}$$
$$2Al^{\cdot\cdot\cdot} + 3S'' + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

Hydrogen persulphides.—If an acid is added to the yellow solution of polysulphides of calcium (p. 481) which contains CaS_2 and probably CaS_5, sulphuretted hydrogen is evolved, and white colloidal sulphur is formed, slowly depositing as milk of sulphur: $CaS_2 + 2HCl = CaCl_2 + H_2S + S$. Scheele (1777) found, however, that if the calcium sulphide solution is poured in a thin stream into cold, fairly concentrated hydrochloric acid, with constant stirring, a yellow oil separates, which Thenard (1832) regarded as **hydrogen persulphide**, H_2S_2, analogous to H_2O_2. A piece of litmus paper placed in the liquid is bleached (EXPT. 182). The oil, which may be separated by a tap-funnel, has a pungent smell, its sp. gr. is 1·7; it is soluble in benzene and carbon disulphide, but is sparingly soluble in, and is decomposed by, alcohol. It slowly decomposes spontaneously, especially on warming, into sulphuretted hydrogen and a residue of sulphur. If sealed up in a bent tube, liquid H_2S collects in one limb, cooled in a freezing mixture, and sulphur remains in the other. The formula of the oil is, therefore, H_2S_x, but its composition is variable, since the sulphur formed on decomposition dissolves in the remaining persulphide. Some chemists considered it to be H_2S_5, but more recent work shows that it is a solution of sulphur in H_2S_2 and H_2S_3.

Sabatier (1885) separated the crude persulphide into fractions by distillation under reduced pressure; under 40–100 mm. pressure the chief fraction has a composition intermediate between H_2S_2 and H_2S_3. Sabatier concluded that it was H_2S_2 + dissolved sulphur. Bloch and Höhn (1908), by using glass vessels treated with hydrochloric acid to remove alkali (which decomposes the persulphide), separated the crude oil by distillation under reduced pressure into two volatile fractions. In the first receiver, **hydrogen trisulphide**, a pale yellow liquid, sp. gr. 1·496, b.-pt. 43–50°/4·5 mm., m.-pt. – 52–53°, collected; and in a further, strongly cooled receiver, **hydrogen disulphide**, H_2S_2, a yellow liquid, sp. gr. 1·376, b.-pt. 74–75°, quickly decomposed by water and alkalies, was obtained. These are supposed to undergo intramolecular change, so that the liquids contain different molecules in equilibrium (p. 497):

$$S{:}S\Big\langle{}^{H}_{H} \rightleftharpoons HS{\cdot}SH \text{ ; } S{:}S{:}S\Big\langle{}^{H}_{H} \rightleftharpoons S{:}SH{\cdot}SH \rightleftharpoons HS{\cdot}S{\cdot}SH.$$

Halogen compounds of sulphur.—The following halogen compounds of sulphur are known:

$$SF_6 \text{ ; } S_2Cl_2,\ SCl_2(?),\ SCl_4 \text{ ; } S_2Br_2.$$

Sulphur burns spontaneously in fluorine, producing a colourless gas, **sulphur hexafluoride,** SF_6 (Moissan and Lebeau, 1900). This is of interest as an example of the maximum valency of sulphur, viz., 6. The gas is chemically inert, like nitrogen, but is decomposed by boiling sodium: $SF_6 + 8Na = Na_2S + 6NaF$. Its relative density is 73; it solidifies at − 55°. Even fused caustic potash and ignited lead chromate or copper have no action upon it; H_2S is decomposed by SF_6, with formation of HF and S.

Sulphur monochloride, S_2Cl_2, is prepared by passing dry chlorine over sulphur fused in a retort (Thomson, 1804). A reddish-yellow liquid distils over into a cooled receiver (Fig. 265). By rectification of this a clear amber-coloured liquid, sp. gr. 1·706, boiling at 138°, is obtained. This solidifies at − 80°. Sulphur monochloride has a vapour density of 67·6, which corresponds with S_2Cl_2 ($\Delta = 67{\cdot}0$). Sulphur monochloride fumes in moist air, and has a most disagreeable pungent odour. The stoppers of bottles in which it is kept become coated with sulphur owing to this hydrolysis:

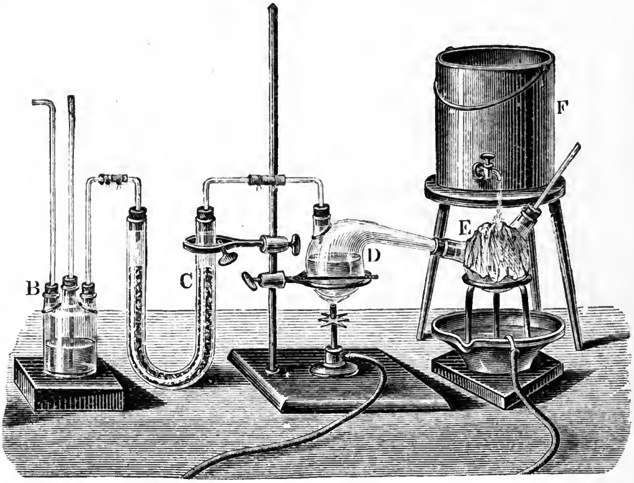


FIG. 265.—Preparation of Sulphur Monochloride.

$$2S_2Cl_2 + 3H_2O = 4HCl + 2S + H_2S_2O_3.$$

The liquid itself is only slowly decomposed by water; hydrochloric acid and sulphur are formed, together with various oxy-acids of sulphur (*e.g.*, thiosulphuric acid, $H_2S_2O_3$, pentathionic acid, $H_2S_5O_6$, etc.). Metals decompose it on heating, forming chlorides and sulphides. S_2Cl_2 dissolves sulphur readily (66 per cent.), and the solution is used in vulcanising rubber (p. 477)

If S_2Cl_2 is saturated with Cl_2 at − 22°, a yellowish-brown liquid is formed, which is **sulphur tetrachloride,** SCl_4. This freezes to a yellowish-white solid, melting at − 31°. On taking the liquid out of the freezing mixture, it decomposes into S_2Cl_2 and Cl_2. Stable double compounds, *e.g.*, $2AlCl_3,SCl_4$, are known. The liquid formed by saturating S_2Cl_2 with Cl_2 at the ordinary temperature was considered to be the dichloride, SCl_2, but is probably a solution of SCl_4 in S_2Cl_2. Double compounds corresponding with the dichloride, *e.g.*, $AsCl_3,SCl_2$, however, are known. **Sulphur monobromide,** SBr, or S_2Br_2, is a garnet-red liquid, b.-pt. 57°/0·2 mm., m.-pt. − 46°, obtained by heating sulphur with bromine in a sealed tube.

EXERCISES ON CHAPTER XXV

1. How would you prove experimentally that all the different modifications of sulphur consist of the same chemical element ? It is sometimes said that, like oxygen and ozone, they contain different amounts of energy : how could this be tested ?

2. From what sources is sulphur obtained ? What varieties of sulphur exist, how are they prepared, and what are their properties ?

3. How is pure hydrogen sulphide prepared ? Give a general account of the action of the gas on solutions of metallic salts. How is its formula established ?

4. How are the persulphides of hydrogen obtained ? Point out the resemblances and differences between hydrogen peroxide, H_2O_2, and hydrogen persulphide, H_2S_2.

5. Describe the preparation and properties of the halogen compounds of sulphur. What light do these compounds throw on the valency of sulphur ?

6. Discuss the allotropy of sulphur from the point of view of the phase rule.

CHAPTER XXVI

THE OXYGEN COMPOUNDS OF SULPHUR

Oxygen compounds of sulphur.—The following **oxides of sulphur** are known :

Sulphur sesquioxide, S_2O_3 : possibly the anhydride of **hyposulphurous acid,** $H_2S_2O_4$;
Sulphur dioxide, SO_2 : the anhydride of **sulphurous acid,** H_2SO_3 ;
Sulphur trioxide, SO_3 : the anhydride of **sulphuric acid,** H_2SO_4 ;
Sulphur heptoxide, S_2O_7 : the anhydride of **persulphuric acid,** $H_2S_2O_8$.

A large number of **oxy-acids of sulphur** are known, either in the free state or in salts :

Hyposulphurous acid,	$H_2S_2O_4$	**Dithionic acid,**	$H_2S_2O_6$
Sulphurous acid,	H_2SO_3	**Trithionic acid,**	$H_2S_3O_6$
Sulphuric acid,	H_2SO_4	**Tetrathionic acid,**	$H_2S_4O_6$
Thiosulphuric acid,	$H_2S_2O_3$	**Pentathionic acid,**	$H_2S_5O_6$
Pyrosulphuric acid,	$H_2S_2O_7$	**Hexathionic acid,**	$H_2S_6O_6$
Persulphuric acid,	$H_2S_2O_8$		
Permonosulphuric acid, or Caro's acid,	H_2SO_5		

SULPHUR DIOXIDE.

Sulphur dioxide, SO_2.—Homer (B.C. *c.* 1100–900) refers to the use of burning sulphur in fumigation, and Pliny states that the fumes were also used for purifying cloth (*i.e.*, bleaching). The alchemists thought the pungent fumes were oil of vitriol but Stahl (1702) showed that they gave peculiar salts with alkalies, and since they stood halfway between sulphuric (vitriolic) acid and sulphur (the latter regarded as sulphuric acid + phlogiston), he called the acid *phlogisticated vitriolic acid.* Priestley (1774) obtained the pure gas by heating concentrated sulphuric acid with mercury, and collected it over mercury. He called it *vitriolic acid air.* Its composition was ascertained by Lavoisier in 1777 by burning sulphur in a measured volume of oxygen ; it is **sulphur dioxide,** SO_2.

The combustion of sulphur.—When roll sulphur is heated in air it fuses, and as the temperature rises a very gentle combustion begins, accompanied by a faint glow, visible only in a dark room. This is due to the oxidation of sulphur vapour, which comes off appreciably at about 230°. At about 360° in air (275–280° in oxygen) the sulphur ignites, and burns with a blue flame, producing **sulphur dioxide,** SO_2, and a little solid **sulphur trioxide,** SO_3, which renders the gas cloudy. Sulphur dioxide also becomes cloudy in a strong beam of light (Tyndall effect, p. 7), owing to the decomposition into fine particles of SO_3 and sulphur : $3SO_2 \rightleftharpoons 2SO_3 + S$. The reaction is reversible, and the gas becomes clear again on standing in the dark.

Sulphur burns in a confined volume of oxygen or air without causing appreciable change of volume, *i.e.*, *sulphur dioxide contains its own volume of oxygen* (Priestley, 1772).

EXPT. 183.—A small piece of sulphur lying in a platinum spoon is ignited in dry oxygen gas confined over *dry* mercury in the apparatus shown in Fig. 266, by means of a piece of fine platinum wire heated electrically in contact with the sulphur. When the apparatus is cool it is found that the mercury levels are practically unchanged. There is a very slight *contraction* due (i) to the formation of a little solid SO_3; (ii) to the greater compressibility of SO_2 as compared with O_2.

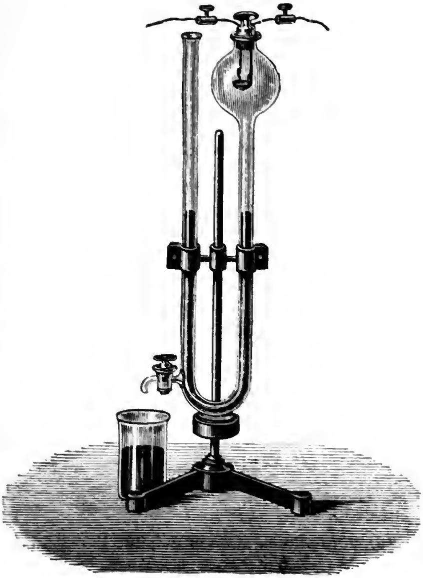


FIG. 266.—Volumetric Composition of Sulphur Dioxide.

The **normal density** of sulphur dioxide is 2·9266, hence its **relative density** (H = 1) is $2·9266 \div 0·09 = 32·5$. The molecular weight is therefore *approximately* $32·5 \times 2 = 65·0$. But the above experiment shows that the molecular weight of the gas contains a molecular weight of oxygen, $O_2 = 32$, hence its formula is S_xO_2. The remainder, $65 - 32 = 33$, is the weight of sulphur. But the atomic weight of sulphur is 31·81, hence the formula is SO_2. The *exact* molecular weight is therefore $31·8 + (2 \times 15·88) = 63·56$ (H = 1).

Sulphur dioxide is prepared on the large scale by the combustion of native sulphur, or of iron pyrites, in a current of air in special burners (*cf.* p. 503). It is used in bleaching wool and straw and as a disinfectant. The largest proportion is used directly in the manufacture of sulphuric acid.

Preparation of sulphur dioxide.—In the laboratory the gas is usually made by the **reduction of sulphuric acid.** If concentrated sulphuric acid is heated with copper, mercury, silver, sulphur, or charcoal, it is reduced, and sulphur dioxide is formed:

$$2H_2SO_4 + Cu = 2H_2O + CuSO_4 + SO_2;$$
$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2;$$
$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2;$$
$$S + 2H_2SO_4 = 3SO_2 + 2H_2O;$$
$$C + 2H_2SO_4 = 2SO_2 + 2H_2O + CO_2.$$

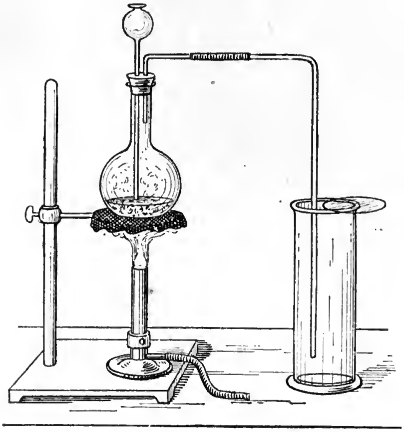


FIG. 267.—Preparation of Sulphur Dioxide.

EXPT. 184.—About 100 gm. of copper turnings are covered with concentrated sulphuric acid in a flask fitted with a thistle funnel (Fig. 267), and heated on wire gauze. The mixture becomes very dark, and gas is evolved with effervescence. When this occurs the flame is removed. The gas is collected by downward displacement (density 2·26 times that of air), or over mercury. After cooling, the residue in the flask is warmed with water, the solution filtered, evaporated, and set aside. Deep blue crystals of **copper sulphate,** $CuSO_4,5H_2O$ (*blue vitriol*), separate. Some black, insoluble cuprous sulphide, Cu_2S, is always produced in the reaction (p. 812).

A more convenient method of preparation is to drop concentrated sulphuric acid into a saturated solution of sodium hydrogen sulphite ("bisulphite"): $NaHSO_3+H_2SO_4 = NaHSO_4 + H_2O + SO_2$.

The gas is most conveniently obtained from the liquid, which is sold in glass siphons (Fig. 268). By inverting these, the liquid is delivered.

FIG. 268.—Liquid Sulphur Dioxide Siphon.

Properties of sulphur dioxide.—Sulphur dioxide is a colourless **gas,** 2·264 times heavier than air.

It has a choking smell, well known as that of burning sulphur, and is poisonous. It does not support combustion in the ordinary sense, but potassium takes fire spontaneously in the gas:

$$4K + 3SO_2 = K_2SO_3 \text{ (sulphite)} + K_2S_2O_3 \text{ (thiosulphate)}.$$

Finely-divided tin and iron also burn in the gas when warmed, forming mixtures of oxides and sulphides. A little lead dioxide in a deflagrating spoon, when warmed and introduced into the gas, becomes incandescent, and forms white lead sulphate: $PbO_2 + SO_2 = PbSO_4$.

When exposed to 2 atm. pressure at 15°, SO_2 forms a colourless **liquid,** b.-pt. – 10·09°; on rapid evaporation, this freezes to a snow-like **solid,** m.-pt. – 76°. The critical temperature is 152·7°, the critical pressure 77·95 atm. The liquid, sp. gr. 1·434 at 0°, readily dissolves iodine, sulphur, phosphorus, resins, and some salts. The solutions of the latter conduct the electric current feebly, so that the solvent has slight ionising properties.

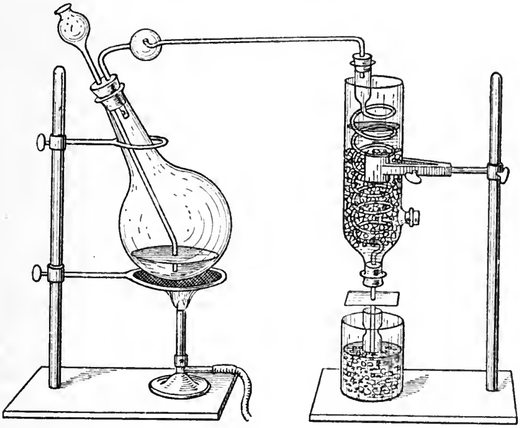


FIG. 269.—Liquefaction of SO_2 by Cooling.

The **ionising power** of a solvent depends on its dielectric constant. Water, with a **dielectric constant** of 81, is a good ionising solvent; benzene (2·3) and sulphur dioxide (13·75) are poor ionising solvents; alcohol (26) occupies an intermediate position.

EXPT. 185.—**Liquid SO_2** is easily prepared by passing the gas through a glass spiral immersed in a mixture of pounded ice and salt (Fig. 269). The liquid is collected in a strong tube with the neck drawn off, immersed in freezing mixture. The neck may be sealed whilst the tube remains cooled, and the liquid preserved.

Sulphurous acid.—Sulphur dioxide is freely soluble in water, forming a liquid smelling strongly of the gas, and acid to litmus. It probably contains the unstable **sulphurous acid,** H_2SO_3, but the latter has never been isolated. On warming, sulphur dioxide is evolved. When the saturated solution is strongly cooled, crystals of the **hydrate,** $SO_2,7H_2O$, separate. The solution when heated in a sealed tube at 150° deposits sulphur:

$$3H_2SO_3 = 2H_2SO_4 + H_2O + S \ (cf.\ 3SO_2 = 2SO_3 + S).$$

The solution of sulphurous acid possesses **bleaching properties;** moistened wool, straw for hats, and other materials which would be injured by chlorine, are bleached on exposure to sulphur dioxide, or the fumes of burning sulphur. This fact, which was known to Paracelsus, has been explained by two different theories: (i) the formation of colourless addition compounds with the colouring matters; (ii) the reduction of the colours to colourless compounds, possibly by nascent hydrogen: $SO_2 + 2H_2O = H_2SO_4 + 2H$.

EXPT. 186.—Add a few drops of fuchsine ("magenta") solution to a solution of sulphur dioxide: the red colour is discharged. Boil with dilute sulphuric acid: the colour is restored.

EXPT. 187.—To a tincture of red cabbage, prepared by soaking the dry leaves in alcohol, add sulphurous acid, and neutralise with soda; the colour is discharged. If an acid is now added a red colour is formed. Red roses may be bleached by wetting them, and suspending in a bell-jar over burning sulphur; on dipping the flowers into dilute sulphuric acid the colour is restored.

Sulphurous acids and sulphites are **reducing agents;** they liberate iodine from potassium iodate:

$$2KIO_3 + 5SO_2 + 4H_2O = I_2 + 2KHSO_4 + 3H_2SO_4.$$

The titration of the liberated iodine serves as a means of **estimation of** SO_2 in flue-gases, or sulphites in solution. With excess of sulphur dioxide, the colour of the iodine again disappears: $I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$. Titration with iodine may also be used in the estimation, but the concentration of SO_2 in the solution should not exceed 0·04–0·05 per cent. (Bunsen). The solution of SO_2 readily absorbs atmospheric oxygen; the rate of oxidation is greatly reduced by the addition of glycerin or mannitol.

Titoff (1903) concluded that in perfectly pure water no oxidation would occur; oxidation is due to traces of iron and copper salts in all water, which act as catalysts. Even 1 gm. atom of $Cu^{\cdot\cdot}$ in 10^6 litres exerts an appreciable influence. Organic substances probably form complex compounds with the metal ions, their action as **negative catalysts** therefore consists in their capability of destroying the positive catalysts ($Cu^{\cdot\cdot}$, etc.).

Sulphur dioxide decolorises a solution of potassium permanganate:

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

Sulphites.—Sulphurous acid is **dibasic,** and forms two series of salts :

Acid sulphites.	**Normal sulphites.**
$KHSO_3$	K_2SO_3
$NaHSO_3$	$KNaSO_3$
$Ca(HSO_3)_2$	$CaSO_3$

EXPT. 188.—Divide a solution of caustic soda into two equal parts. Saturate one with SO_2, producing a solution of **sodium hydrogen sulphite,** $NaHSO_3$. This is acid, owing to dissociation of the HSO_3 ion ($HSO_3' \rightleftharpoons SO_3'' + H^{\cdot}$). Mix this with the other half of the caustic soda, and evaporate. Crystals of normal **sodium sulphite,** $Na_2SO_3,7H_2O$, are produced on cooling.

Sodium sulphite forms a slightly alkaline solution, owing to hydrolysis : $SO_3'' + H_2O \rightleftharpoons HSO_3' + OH'$. It gives a white precipitate of **barium sulphite,** *soluble in hydrochloric acid,* on addition of barium chloride : $Ba^{\cdot\cdot} + SO_3'' \rightleftharpoons BaSO_3$ (dissd.) $\rightleftharpoons BaSO_3$ (ppd.). If chlorine- or bromine-water is added to the solution in hydrochloric acid, oxidation occurs, and a white precipitate of **barium sulphate,** $BaSO_4$, *insoluble in hydrochloric acid,* is formed :

$$SO_3'' + H_2O + Cl_2 = SO_4'' + 2Cl' + 2H^{\cdot}.$$

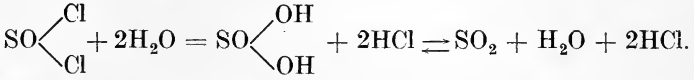
Sulphur dioxide, when passed through lime-water, gives a white precipitate of **calcium sulphite,** $CaSO_3$.

If a solution of sodium hydrogen sulphite is mixed with alcohol, the salt $NaHSO_3$ is precipitated, but if it is boiled and evaporated, a new salt, $Na_2S_2O_5$, called **sodium metabisulphite** (*i.e.*, $Na_2O,2SO_2$) is formed, which is used in photography. On heating dry sodium sulphite, the sulphate and sulphide are formed : $4Na_2SO_3 = Na_2S + 3Na_2SO_4$. $NaHSO_3$ on heating first produces Na_2SO_3, H_2O, and SO_2, and the Na_2SO_3 then decomposes as above.

Thionyl chloride.—If sulphur dioxide is passed over phosphorus pentachloride, PCl_5, a liquid is formed which on fractional distillation is separated into **thionyl chloride,** $SOCl_2$ (b.-pt. 78°), and phosphorus oxychloride, $POCl_3$ (b.-pt. 107°) : $SO_2 + PCl_5 = SOCl_2 + POCl_3$. $SOCl_2$ is also formed by the addition of sulphur to chlorine monoxide at $-12°$: $Cl_2O + S = SOCl_2$. It is manufactured by adding sulphur trioxide to sulphur chloride at 75–80°, and passing a stream of chlorine through the mixture to reconvert the separated sulphur into the chloride :

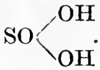
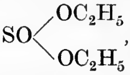
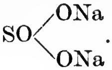
$$SO_3 + S_2Cl_2 = SOCl_2 + SO_2 + S.$$

Thionyl chloride, *i.e.*, the chloride of the radical *thionyl,* $SO\!<$, is a colourless liquid, sp. gr. 1·675 at 0°. It fumes in moist air, and is decomposed by water, forming hydrochloric and sulphurous acids; it is an **acid chloride** *i.e.*, sulphurous acid with univalent hydroxyl replaced by chlorine:

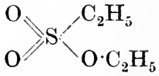
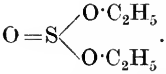


$$SO\begin{cases}Cl\\Cl\end{cases} + 2H_2O = SO\begin{cases}OH\\OH\end{cases} + 2HCl \rightleftharpoons SO_2 + H_2O + 2HCl.$$

Thionyl bromide, $SOBr_2$, is a red liquid, b.-pt. 68°/40 mm., formed by acting on $SOCl_2$ with KBr. With $SOCl_2$ and HBr a pale yellow liquid, **thionyl chlorobromide,** SOClBr, is also formed, b.-pt. 115°. **Thionyl fluoride,** SOF_2, is a colourless gas obtained by heating $SOCl_2$ and arsenic fluoride, AsF_3. It boils at $-32°$, and forms with dry ammonia the compounds $2SOF_2,5NH_3$ and $2SOF_2,7NH_3$.

The constitution of sulphurous acid.—The formation of sulphurous acid by the action of water on thionyl chloride suggests that it has the **symmetrical formula**  $SO\begin{cases}OH\\OH\end{cases}$. By the action of thionyl chloride on alcohol **symmetrical diethyl sulphite,**  $SO\begin{cases}OC_2H_5\\OC_2H_5\end{cases}$, b.-pt. 161°, is formed, which is hydrolysed when boiled with caustic soda, yielding alcohol and sodium sulphite. The formula of the latter would thus appear to be symmetrical:  $SO\begin{cases}ONa\\ONa\end{cases}$.

By the action of sodium sulphite on ethyl iodide, a compound having the same composition as diethyl sulphite is obtained: $Na_2SO_3 + 2C_2H_5I = (C_2H_5)_2SO_3 + 2NaI$.

This is, however, not symmetrical diethyl sulphite, since it boils at 207°. When boiled with caustic soda it yields **sodium ethylsulphonate,** $NaC_2H_5SO_3$, a salt of **ethylsulphonic acid,** $C_2H_5SO_3H$. In the latter the ethyl group, C_2H_5, is almost certainly directly attached to the sulphur atom, since the compound is formed by oxidising **mercaptan,** or ethyl hydrogen sulphide, C_2H_5SH, with dilute nitric acid. The liquid boiling at 207° also, probably, contains an ethyl group directly attached to the sulphur atom, since it is derived from the sulphonic acid; it has an unsymmetrical formula:  $\begin{matrix}O\\O\end{matrix}\!\!>S\begin{cases}C_2H_5\\O{\cdot}C_2H_5\end{cases}$, whilst the first compound is symmetrical:  $O=S\begin{cases}O{\cdot}C_2H_5\\O{\cdot}C_2H_5\end{cases}$. These two compounds, which have the same percentage composition, and the same molecular weight, but different properties, are called **meatmeric compounds,** or **metamers,** and the phenomenon of the existence of such compounds is called **metamerism.** Isomerism is explained by the different modes of arrangement of the atoms in the molecules, *i.e.*, different **structures.**

Since sulphurous acid appears to have two different formulæ according to the reactions by which it is produced, viz.,

unsymmetrical **symmetrical**

it is assumed that *both* forms exist in equilibrium in a solution of the acid, and are readily converted into each other, so that according to the reagent presented to the acid, the latter appears to have sometimes one and sometimes the other formula. This property is called **dynamic isomerism,** or **tautomerism.** The two forms are called **dynamic isomers.**

SULPHUR TRIOXIDE AND SULPHURIC ACID.

Sulphur trioxide.—**Sulphur trioxide,** SO_3, is produced by the direct union of the gaseous dioxide with ozone (Brodie): $3SO_2 + O_3 = 3SO_3$. It is a white crystalline solid. It is also produced when a mixture of the dioxide and oxygen, or air, is passed over a catalyst, such as platinised asbestos heated to 500° (P. Phillips, 1831), or the oxides of iron, copper, chromium, or vanadium heated to 600–700° (Wöhler): $2SO_2 + O_2 \rightleftarrows 2SO_3$. A state of **equilibrium** is set up, since the reaction is reversible.

At 400°, 2 per cent. of SO_3 is decomposed; at 700°, 40 per cent. In a mixture of SO_2 and air, such as is obtained by burning pyrites (p. 503), containing by volume 7 per cent. of SO_2, 10·4 per cent. of O_2, and 82·6 per cent. of N_2, the following percentages of SO_2 are oxidised to SO_3 in equilibrium: at 434°, 97; at 550°, 85; at 645°, 60. The reverse change, $2SO_3 \rightarrow 2SO_2 + O_2$, is favoured by rise of temperature, since it absorbs heat (p. 355). The direct change $2SO_2 + O_2 = 2SO_3 + 45$ kg. cal. does not proceed in presence of platinum at an appreciable rate below 400°, on account of the slowness of reaction at lower temperatures. The two conflicting effects of temperature on the yield are balanced in practice by working at 400–450°, which is the *optimum* temperature with platinum as a catalyst, and using excess of oxygen in the form of air, as described.

EXPT. 189.—Pass a mixture of SO_2 and O_2 through sulphuric acid to dry it, and then over platinised asbestos heated in a hard glass tube, *c* (Fig. 270). Dense white fumes are produced, which condense in the cooled dry receiver, *d*, to a colourless liquid, which gradually solidifies. This is **sulphur trioxide.**

The trioxide is also produced by heating concentrated sulphuric acid with phosphorus pentoxide: $H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$, or most conveniently by distilling **fuming sulphuric acid** (*q.v.*):

$H_2S_2O_7 \rightleftharpoons H_2SO_4 + SO_3$. If sodium hydrogen sulphate is heated to 300° it forms the **pyrosulphate,** and this evolves sulphur trioxide at a bright red heat: $2NaHSO_4 = Na_2S_2O_7 + H_2O$; $Na_2S_2O_7 = Na_2SO_4 + SO_3$. The formation of a "volatile salt" on distilling fuming sulphuric acid was described by "Basil Valentine" (p. 29), and by Bernhardt in 1775.

Sulphur trioxide appears to exist in **two modifications.** The liquid, b.-pt. 46°, at first obtained solidifies on cooling to **transparent crystals,** melting at 14·8°, sp. gr. 1·97 at 20°. The lowering of vapour pressure of a solution of this form, called α-SO_3, shows that it has the formula SO_3. If α-SO_3 is allowed to stand some time, in presence of a trace of moisture, it forms silky, **asbestos-like crystals,** the molecular weight of which, in solution in $POCl_3$, corresponds with S_2O_6. This is β-SO_3. At 50° the β-form changes slowly into the α-form.

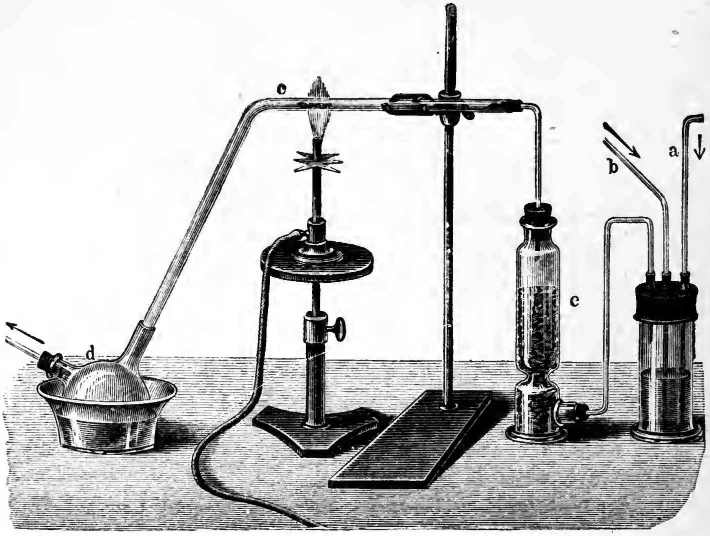


FIG. 270.—Formation of Sulphur Trioxide.

The vapour density of sulphur trioxide corresponds with the formula SO_3. When passed through a red-hot tube it decomposes, giving 2 vols. of SO_2 and 1 vol. of O_2, which do not recombine on cooling except in the presence of a catalyst: $2SO_3 = 2SO_2 + O_2$. The solid absorbs moisture with avidity from the air, giving off dense white fumes composed of droplets of **sulphuric acid**: $H_2O + SO_3 = H_2SO_4$. It dissolves in water with a loud hissing noise, and considerable evolution of heat. Sulphur trioxide dissolves readily in concentrated sulphuric acid; the fuming acid so obtained solidifies on cooling to colourless crystals of **pyrosulphuric acid,** $H_2S_2O_7$, m.-pt. 35°. Sulphur trioxide reacts violently with baryta, the mass becoming incandescent: $SO_3 + BaO = BaSO_4$.

Manufacture of sulphur trioxide and sulphuric acid by the contact process.—Repeated attempts were made to adapt Phillips's **contact process** to large-scale working, but it was found that the platinum rapidly became inactive ("poisoned"), and the conversion of SO_2 into SO_3 ceased. After years of unremitting work, the Badische Soda and Aniline Co., of Ludwigshafen in Germany, found that the poisoning is due to impurities, especially arsenious oxide and dust, in the gases from the pyrites burners, and that if these impurities are got rid of by blowing a jet of steam into the burner gas, allowing to settle, cooling, and passing through coke filters drenched with concentrated sulphuric acid until no fog is seen by a powerful beam of light ("optically clear" gas), the platinum retains its activity for an indefinite period.

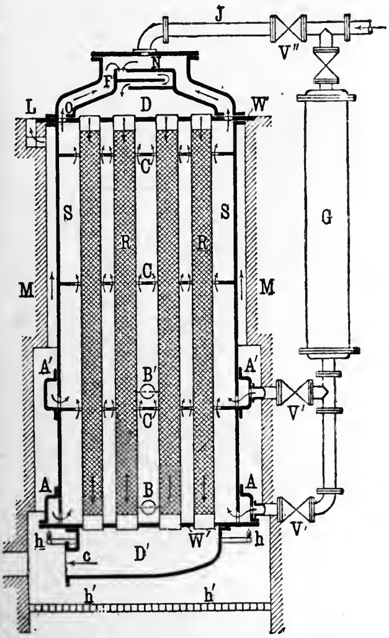


FIG. 271.—Contact Chamber of Badische Process.

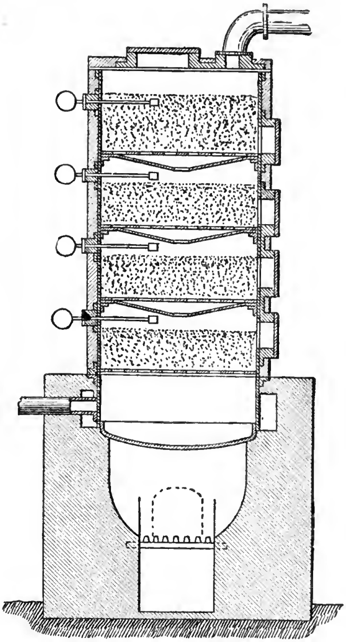


FIG. 272.—Schröder-Grillo Contact Chamber.

In the **Badische process** the purified gas is passed into a **converter** (Fig. 271), consisting of an iron cylinder with inlet and outlet pipes. Inside are vertical iron tubes packed with platinised asbestos. Twice the theoretical amount of oxygen is present in the gas (in the form of air), and the apparatus is heated by the gas burners, *h*, to start the reaction: this afterwards proceeds automatically. By letting the incoming gas sweep over the outside of the hot tubes in which the reaction occurs, no external heating is needed, since a considerable amount of heat is evolved, and the process goes on continuously at 400–450°.

The sulphur trioxide cannot be **absorbed** from the issuing gases by passing through water, as a dense fog of minute droplets of H_2SO_4 is thus formed, which cannot be condensed. The gas is therefore passed into 97–99 per cent. sulphuric acid in iron towers; the concentrated acid rapidly absorbs the SO_3, producing **fuming sulphuric acid,** or **oleum**; or, if a regulated stream of water is admitted, the 97–99 per cent. acid is continuously increased in quantity by the reaction $SO_3 + H_2O = H_2SO_4$ occurring in the liquid acid.

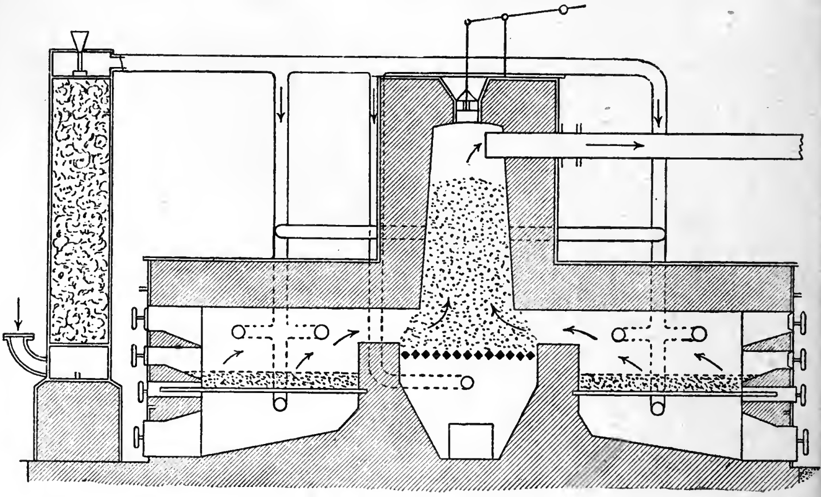


FIG. 273.—Mannheim Contact Process.

In the **Schröder-Grillo process,** which has been extensively worked in England and America, the catalyst is prepared by moistening Epsom salt, $MgSO_4,7H_2O$, with a solution of platinum chloride, and heating. The salt loses water, and swells up to a voluminous mass, on which the platinum is very finely divided. This contact mass is put on shelves in iron converters, lagged outside (Fig. 272), and when the process is once started it goes on without external heating.

The **Tenteleff process** utilises a catalyst composed of asbestos "sponge-cloths," soaked in platinic chloride, and the latter reduced by formaldehyde. These are ignited, and a number of superposed cloths are fitted into an iron frame, 3 ft. by 2 ft., interposed in the gas current. The temperature is 450–500°. This arrangement is often used in finishing off the conversion in the Mannheim process (*q.v.*).

The **Mannheim process** utilises burnt pyrites (Fe_2O_3 and CuO) as the contact mass. This is filled into a rectangular tower, the lower part of which communicates with two pyrites burners, to which air dried in a sulphuric acid tower is supplied (Fig. 273). The hot gases pass directly to the iron oxide shaft, and, on account of the higher temperature, only about 60 per cent. of the SO_2 is converted into SO_3. The arsenious oxide in the burner gases is kept back in the oxide of iron as ferric arsenate, and after the SO_3 has been absorbed from the exit gas by sulphuric acid, the gas is filtered through scrubbers of coke soaked in concentrated sulphuric acid, reheated, and passed to a Tenteleff converter to finish the conversion. This process has also been used fairly extensively in England, but is not so economical as the Schröder method.

Fuming sulphuric acid, or **oleum,** is an oily liquid, often coloured brown by organic matter, but colourless when pure, which emits thick white fumes in moist air. It may be kept in mild-steel drums, but cracks cast iron (which resists the action of ordinary concentrated sulphuric acid). It is made with different contents of free SO_3, *i.e.*, SO_3 in excess of the amount required to form H_2SO_4. The strongest product contains 60 per cent. of free SO_3, and emits very dense fumes. The hydrates H_2O,SO_3 (H_2SO_4, or **monohydrate,** m.-pt. 10°), H_2SO_4,H_2O or $SO_3,2H_2O$ (m.-pt. −8°), $H_2O,2SO_3$ or $H_2S_2O_7$ (**pyrosulphuric acid,** m.-pt. 35°), and $H_2SO_4,4H_2O$ (m.-pt. − 25°) are known. Acids containing more than 60 and less than 40 per cent. of free SO_3 are liquid at the ordinary temperature; the others are solid. Oleum is used in organic chemistry to prepare **sulphonic acids,** RSO_3H (p. 511), and in adding to mixtures of nitric and sulphuric acids used for **nitration** (p. 569). It is added to ordinary acid to increase its concentration.

Sulphuric acid, H_2SO_4.—Moistened flowers of sulphur, when exposed to air, are slowly oxidised, and a little sulphuric acid is formed. Sulphurous acid in solution oxidises slowly when exposed to air: $2H_2SO_3 + O_2 = 2H_2SO_4$. Oxidation occurs more rapidly when hydrogen peroxide is shaken in a jar of sulphur dioxide: $SO_2 + H_2O_2 = H_2SO_4$. Chlorine water and bromine water also oxidise sulphurous acid: $H_2SO_3 + H_2O + Cl_2 = H_2SO_4 + 2HCl$.

Sulphuric acid, or **oil of vitriol**, is mentioned by the Latin Geber, who obtained it by distilling *green vitriol*, *i.e.*, ferrous sulphate: $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$; with moisture, the SO_3 forms H_2SO_4. In 1666 Lemery and Le Févre obtained the acid by deflagrating a mixture of sulphur and nitre over a dish of water under a glass bell, and a small works using this process was established in 1740 by Ward, at Richmond. The acid obtained was called oil of vitriol *per campanum.* Roebuck, in 1746, replaced the fragile glass vessels by **lead chambers,** 6 ft. wide, at Prestonpans, and these were enlarged in later works. These chambers were introduced into France in 1769 by the Englishman Holker, and in 1774 La Folie employed a jet of steam in the chamber. A considerable advance was possible after the researches of Clement and Desormes (1793), who pointed out the importance of a current of air in the chambers, and in 1806 these chemists gave a correct interpretation of the reactions occurring in the chambers, particularly the part played by the oxides of nitrogen. A continuous process, in which the sulphur dioxide was produced from sulphur in separate burners, and admitted, together with nitrous fumes, air, and steam, to the chambers, was introduced by Holker into the French works of Chaptal in 1810. The use of pyrites as a source of sulphur dioxide, introduced by Hill, of Deptford, in 1818, and the invention of the Gay-Lussac and Glover towers (*q.v.*) in 1835 and 1859, respectively, led to the modern chamber acid industry.

More than one million tons of sulphuric acid are produced annually by each of the three countries, Great Britain, Germany, and America.

The lead chamber process.—The reactions in the lead chambers occur between sulphur dioxide, oxygen (air), steam (or water-spray), and oxides of nitrogen ("nitrous fumes"). It appears, as was discovered by Clement and Desormes, that an intermediate compound, **nitrososulphuric acid** ("chamber crystals"), is formed and decomposed alternately:

$$(1)\ 2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH)\cdot O\cdot NO$$
$$(2)\ 2SO_2(OH)\cdot O\cdot NO + H_2O = 2H_2SO_4 + N_2O_3.$$

The nitrous fumes, N_2O_3 (or, really, $NO_2 + NO$), thus act over and over again in a cyclic manner, *i.e.*, as a **catalyst** (p. 166).

EXPT. 190.—A dry 6–litre flask, *A*, is fitted with four inlet tubes, as shown in Fig. 274, and a small outlet tube. Three of the tubes are connected with wash-bottles containing concentrated sulphuric acid. One of these is connected with a siphon of liquid SO_2, one to a gas-holder containing oxygen, and the third to a gas-holder containing nitric oxide (p. 578). The fourth tube is connected with a small flask, *B*, containing water, which may be heated, and through which oxygen may be bubbled. A rapid stream of oxygen is first passed through the apparatus. Nitric oxide is then passed in, which at once forms brown fumes of higher oxides of nitrogen. Sulphur dioxide is then passed in at the same rate as the nitric oxide, and, after a short time, a current of oxygen is passed through the hot water in *B* to carry moisture into the globe. White star-shaped crystals of nitrososulphuric acid form on the inside of the flask. The colour of the gases at the same time becomes much paler. Sweep out the gases by a rapid current of dry oxygen, and then boil the water in *B*. When the steam comes in contact with the crystals, these dissolve with effervescence, producing red fumes of oxides of nitrogen.

The liquid in the flask gives a white precipitate ($BaSO_4$) with $BaCl_2$ solution.

On the large scale, lump pyrites is burnt in brick furnaces, called **pyrites burners,** the grates of which are composed of separate square bars which can be turned on their longitudinal axes so as to drop the burnt ore into the ash-pits. The supply of air is carefully regulated by sliding doors above and below the bed of pyrites. Each furnace holds 3–5 tons of ore, and they are arranged in sets of 20–25, with a communicating flue, for each set of chambers. The daily charge for each furnace is 750–1000 lb. of pyrites. Pyrites powder, or " spent oxide "(p. 477), is burnt in rotary kilns, consisting of iron cylinders lined with firebrick, with a series of shelves so arranged that the ore is raked from shelf to shelf until the burnt ore is discharged at the bottom. The rakes are actuated by a revolving air- or water-cooled central shaft.

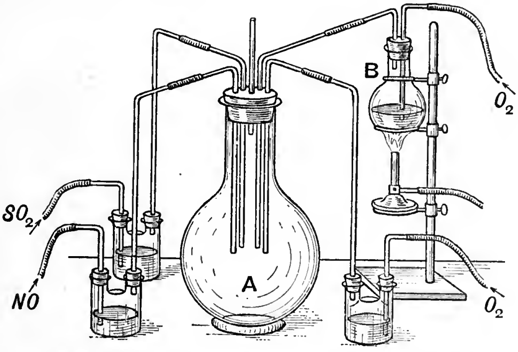


FIG. 274.—Experiment illustrating Reactions in Sulphuric Acid Chambers.

The burner gas (7 per cent. of SO_2, 10 per cent. of O_2, 83 per cent. of N_2) passes to a **dust-catcher,** containing baffle-walls, and then through a **nitre-oven,** in which pots containing sodium nitrate and sulphuric acid are placed. These supply the oxides of nitrogen to make up losses from the plant. About 3 parts of $NaNO_3$ per 100 parts of S burnt as pyrites are required. In modern plants, the oxides of nitrogen are supplied by the oxidation of ammonia (p. 575). From the dust-catcher the gases pass, at 300–400°, into the **Glover**

tower, seen on the right in Fig. 275. This is a lead tower lined with acid-resisting bricks, 20–30 ft. high, and 6–8 ft. diameter, packed with flints resting on an arch. Down this tower two streams of acid, from the tanks seen at the top, are passed. One stream consists of dilute acid (65–70 per cent. H_2SO_4) from the lead chambers; the other consists of stronger acid (78 per cent. H_2SO_4) containing oxides of nitrogen (in the form of nitrososulphuric acid) from the Gay-Lussac tower seen on the left. The functions of the Glover tower are three: (*a*) to cool the burner gases to 50–80° before they enter the chambers; (*b*) to denitrate the acid from the Gay-Lussac tower, by dilution with chamber acid, and heating; (*c*) to concentrate the weak acid to about 78 per cent. H_2SO_4 for sale, or for use in the Gay-Lussac tower, and at the same time provide steam for the chambers. About 25 per cent. of the acid made in the plant is also formed by reactions in the Glover tower.

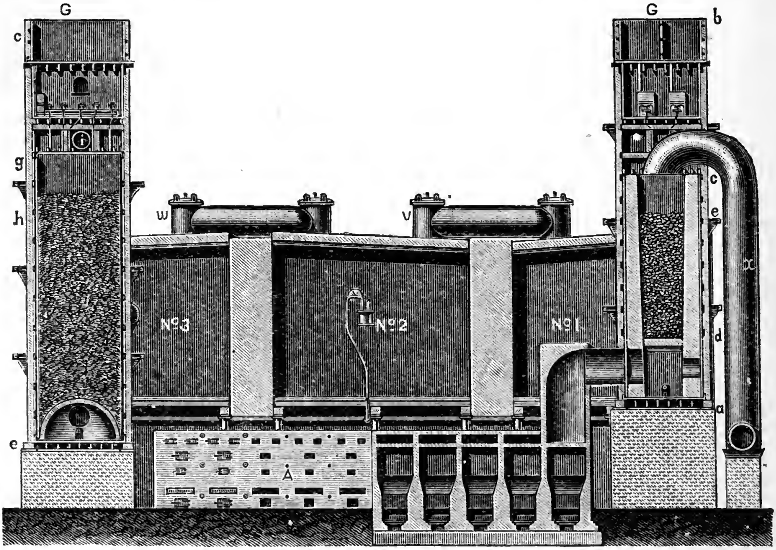


FIG. 275.—Diagram of Sulphuric Acid Chamber Plant, showing end view of three Chambers, Gay-Lussac Tower (left), Glover Tower (right) and Pyrites Burners, *A*.

From the Glover tower the gases now pass, by a lead main seen on the extreme right of Fig. 275, to the first of the set of **lead chambers,** the ends of three of which are shown. These are formed of sheet lead weighing 6–8 lb. per sq. ft., are oblong or square in shape, and dip into large lead saucers with a seal of acid. The chambers are suspended from a wooden or iron frame by lead straps welded on the sides. All joints in the lead sheets are autogenously welded by a hydrogen flame. The capacity of each chamber is 25,000–75,000 cu. ft., and three or four, connected by wide lead pipes, form a set.

Steam, or more usually a fine spray of liquid water from several jets in the roof, is blown into the chamber. Sulphuric acid is produced in the form of a fog of small drops, which settle down into liquid **chamber acid** (65–70 per cent. H_2SO_4) on the floor of the chamber. In modern practice, 10 cu. ft. of chamber space is allowed per lb. of S burnt per twenty-four hours. The capacities of the Glover and Gay-Lussac towers are each about 1 per cent. that of the chambers; the height of the Glover tower does not exceed 30 ft. The conversion of SO_2 to H_2SO_4 reaches 98 per cent.

The gases from the last chamber, containing nitrogen, a little oxygen, most of the oxides of nitrogen in circulation through the plant, and a trace of sulphur dioxide, now pass to the **Gay-Lussac tower,** shown on the left in Fig. 275. This is a lined lead tower, 40–60 ft. high, and 8–15 ft. in diameter, packed with hard coke, and fed with cold Glover acid (78 per cent. H_2SO_4). Its function is to recover the oxides of nitrogen in the exit gases from the chambers. These are absorbed, producing **nitrous vitriol,** containing nitrososulphuric acid equivalent to 1–2 per cent. N_2O_3, which is pumped to the Glover tower for denitration. The waste gas from the Gay-Lussac tower passes to a chimney, which maintains a draught through the whole system.

Theory of the lead chamber process.—The reactions which occur in the chambers are complicated, and still not completely understood. The chief point calling for explanation is the action of the oxides of nitrogen. Berzelius represented this as follows:

$$(1)\ NO_2 + SO_2 + H_2O = H_2SO_4 + NO.$$
$$(2)\ NO + O = NO_2.$$

Davy put forward another explanation, elaborated by Lunge. According to this, **nitrososulphuric acid,** $SO_2(OH){\cdot}O{\cdot}NO$, *i.e.*, sulphuric acid, $SO_2(OH){\cdot}OH$, in which one atom of hydrogen is replaced by the **nitroso-group,** NO, is an intermediate product. This is formed by the action of nitrous anhydride, N_2O_3, traces of which exist in equilibrium with NO and NO_2: $NO + NO_2 \rightleftarrows N_2O_3$:

$$(1)\ 2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH){\cdot}O{\cdot}NO.$$

This does not deposit in crystals, but is at once hydrolysed:

$$(2)\ 2SO_2(OH){\cdot}O{\cdot}NO + H_2O = 2SO_2(OH)_2 + N_2O_3.$$

In the first chamber, where the gases are very pale and an excess of NO is present, the following reactions may occur:

$$2SO_2(OH){\cdot}O{\cdot}NO + SO_2 + 2H_2O = 3SO_2(OH)_2 + 2NO$$
$$2SO_2 + 2NO + 3O + H_2O = 2SO_2(OH){\cdot}O{\cdot}NO.$$

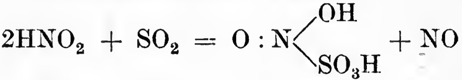
In a more recent theory Lunge (1906) assumes the formation of a hypothetical **sulphonitronic acid,** H_2SNO_5, which then forms nitrososulphuric acid, $HSNO_5$:

(1) $SO_2 + NO_2 + H_2O = H_2SNO_5$.
(2*a*) $2H_2SNO_5 + O = H_2O + 2HSNO_5$.
(2*b*) $2H_2SNO_5 + NO_2 = 2HSNO_5 + NO + H_2O$.

Decomposition of nitrososulphuric acid then occurs:

(3*a*) $2HSNO_5 + H_2O = 2H_2SO_4 + NO + NO_2$.
(3*b*) $2HSNO_5 + SO_2 + 2H_2O = H_2SO_4 + 2H_2SNO_5$.
(3*c*) $H_2SNO_5 = NO + H_2SO_4$.
(4) $NO + O = NO_2$.

Raschig (1887) proposed a different scheme:

(1) 

$$2HNO_2 + SO_2 = O{:}N\Big\langle\begin{matrix}OH\\SO_3H\end{matrix} + NO$$

(2) $H_2SNO_5 = H_2SO_4 + NO$.
(3) $2NO + H_2O + O = 2HNO_2$.

He further supposes that H_2SNO_5 may react with SO_2 to form **hydroxylamine disulphonic acid,** $HO{\cdot}N(SO_3H)_2$, and **nitrylsulphonic acid,** $N(SO_3H)_3$, which may lose sulphonic groups and form hydroxylamine, NH_2OH, and ammonia, NH_3. Traces of the latter are sometimes found in chamber acid. Trautz believes that, to a limited extent, **nitrosodisulphonic acid,** $NO(SO_3H)_2$, may be formed by the action of nitrous acid on sulphurous acid, which is then decomposed by nitrous acid as follows:

$$NO(SO_3H)_2 + 2HO{\cdot}NO = 3NO + 2H_2SO_4.$$

The concentration of sulphuric acid.—The chamber acid (65–70 per cent. H_2SO_4) may be used directly in the manufacture of superphosphates. Unless all the acid is passed through the Glover tower, the remainder of the chamber acid may be concentrated to the strength of Glover tower acid (78 per cent. H_2SO_4) by evaporation in flat lead pans by waste heat from the pyrites burners. The 78 per cent. acid is usually called "brown oil of vitriol," or B.O.V., on account of its colour, due to organic matter. Stronger acid, 93–95 per cent. H_2SO_4, called "rectified oil of vitriol," or R.O.V., is required for many purposes, and is made by concentration of B.O.V. This **concentration,** formerly carried out by heating in glass or platinum retorts, when steam is emitted, is now effected in one of three types of concentration apparatus: the Cascade apparatus, the Kessler apparatus, and the Gaillard tower. In all cases the acid is heated and a current of hot air passed over its surface. The vapours emitted are composed of very weak acid so that the remaining acid increases in strength.

In the **cascade process** the acid is allowed to flow down a series of vitrified silica, or ferro-silicon, dishes, arranged one above the other, with the spout of one discharging into the basin next lower, the whole resting on a kind of staircase of acid-resisting bricks. The acid is heated by a flue below, and hot air sweeps over its surface (Fig. 276). Much of the acid is lost in the form of fumes. From the last dish, which may be of cast iron, the acid flows to a cooler.

In the **Kessler apparatus** the acid flows through a dish, *S*, of Volvic stone (a natural acid-resisting material of volcanic origin, found at Puy-de-Dôme), covered outside with lead, through which hot gas from a coke generator (p. 705) passes (Fig. 277). The dish has ridges, *b*, so as to bring the acid and fire-gas into intimate contact. The concentrated acid runs off to a cooler. The fumes pass through a tower, *R*, containing a number of plates with perforations covered with inverted cups, down which the acid to be concentrated is fed. Much of the fume is here condensed, and the temperature is kept at such a point that steam escapes, but the sulphuric acid remains. The issuing fumes then pass through a lead box packed with graded coke, drenched with concentrated sulphuric acid, which takes out the fine mist of acid droplets.

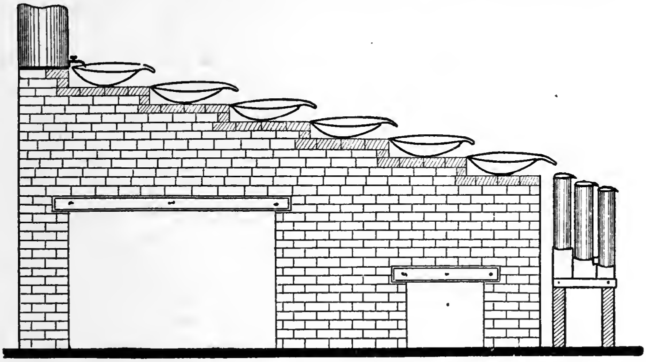


FIG. 276.—Cascade Apparatus for Concentrating Sulphuric Acid.

The **Gaillard tower** (Fig. 278) consists of an empty tower of Volvic stone or acid-resisting brick, from the top of which a fine spray of acid is discharged. In passing down the tower this spray meets a current of hot gas from a coke generator, which enters the tower at the side near the bottom. The acid is concentrated by the hot gas, and runs out from the lead saucer, in which the tower stands, to a cooler. The fumes from the tower are passed through a smaller empty lead tower, called a **recuperator,** down which a portion of the acid to be concentrated is passed, and finally to coke filters. The tower is 60 ft. high and 10 ft. in diameter.

The acid fumes from concentrators may be condensed by means of **electrostatic precipitation** (p. 15). They are passed through a chamber in which lead plates are hung, with lead covered bars hanging vertically between them. These are charged to a potential of 20,000 volts. The acid droplets are attracted to the plates, and the liquid deposited on the latter runs off to collecting tanks, and is returned to the concentrators.

Still more concentrated acid, containing 97–98 per cent. of H_2SO_4, is produced from the 93–95 per cent. acid by heating the latter in **cast-iron pans** by direct fire. The very strongest acid does not attack cast iron, whilst 93–95 per cent. acid dissolves it. The acid is therefore run in a fine stream on to the surface of a large bulk of 98 per cent. acid boiling in a large cast-iron pot provided with a siphon neck opening into it near the bottom. The strong acid is run off continuously from this "swan-neck" as the concentration proceeds. The acid may also be brought to any desired strength by the addition of oleum (sulphuric acid containing SO_3).

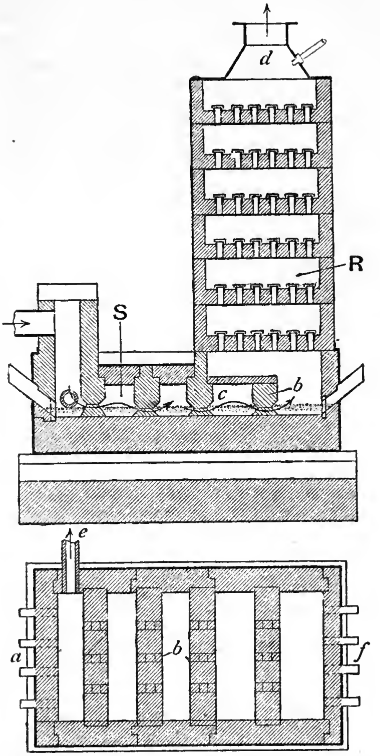


FIG. 277.—Kessler Apparatus for Concentrating Sulphuric Acid.

The purification of sulphuric acid. — Commercial sulphuric acid often contains arsenic trioxide, As_2O_3, in solution, derived from the arsenic in the pyrites. It is **purified** by treating the chamber acid with sulphuretted hydrogen in lead towers or closed agitators. The precipitate of arsenic sulphide, As_2S_3, is filtered off by suction through unglazed earthenware plates, or is removed by flotation (p. 10); a little paraffin, added to the liquid, floats to the surface and carries with it the precipitate. Acid made from sulphur ("brimstone acid") is preferred for the preparation of foods (*e.g.*, glucose, made from starch by boiling with dilute sulphuric acid), although de-arsenicated acid from pyrites is also used.

Properties of sulphuric acid.—Pure sulphuric acid, or **monohydrate,** H_2SO_4, is prepared by adding the requisite amount of SO_3 to 98 per cent. acid. It is an oily liquid which fumes slightly in air, apparently because it contains a little free sulphur trioxide: $H_2SO_4 \rightleftharpoons SO_3 + H_2O$, formed by dissociation in the liquid. This dissociation increases on heating, and the vapour is richer in SO_3 than the residual liquid. It is therefore impossible to obtain pure H_2SO_4 by the ordinary concentration process. The monohydrate freezes in ice and salt, and the crystals then melt at 10°. On boiling, an acid of constant composition, 98·3 per cent. H_2SO_4, comes over at a temperature of 330°, which is usually given as the boiling point of sulphuric acid.

The ordinary concentrated acid, containing about 98 per cent. H_2SO_4, is an oily colourless liquid, of sp. gr. 1·85. It does not fume in the air.

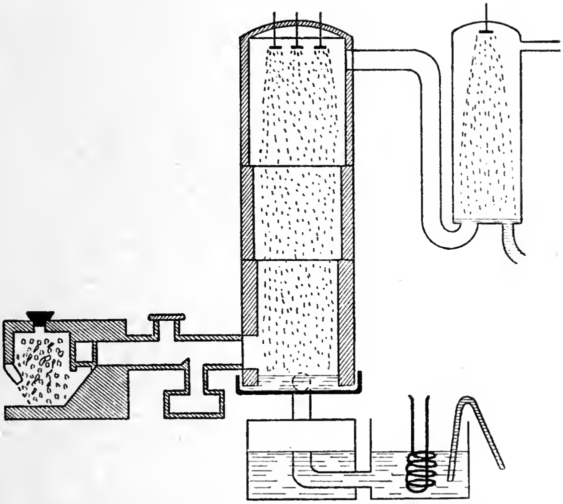


FIG. 278.—Gaillard Tower for Concentrating Sulphuric Acid.

Concentrated sulphuric acid has a **strong affinity for water.** When the acid is mixed with water a considerable amount of heat is given out, and the liquid may boil. In practice, it is always safest to add the acid to the water in a thin stream, with stirring. The water should never be added to the acid. The diluted acid occupies a less volume than its constituents.

If the acid is mixed with snow, cold is produced, because the latent heat of fusion of ice exceeds the heat evolved on mixing the acid with liquid water.

The definite crystalline hydrates, H_2SO_4,H_2O and $H_2SO_4,4H_2O$, are known, and probably exist in a partially dissociated state in the liquid.

The density of pure sulphuric acid is 1·8384 at 15°. The densities of mixtures of the acid with water are given in the table below. It will be seen that 97·7 per cent. acid has a maximum density.

TABLE OF DENSITIES OF SULPHURIC ACID.

Density.	Per cent. H_2SO_4.	Density.	Per cent. H_2SO_4.
1·000	0·09	1·645	72·40
1·075	10·90	1·720	78·92
1·150	20·91	1·780	84·50
1·180	24·76	1·825	91·00
1·240	32·28	1·835	93·43
1·300	39·19	1·841	97·00
1·390	49·06	1·8415	97·70
1·450	55·03	1·840	99·20
1·525	62·06	1·8384	100.00
1·600	68·51		

TABLE OF DENSITIES OF OLEUM.

Density.	Per cent. free SO_3.	Density.	Per cent. free SO_3.
1·888	10	2·020	60
1·920	20	2·018	70
1·957	30	2·008	80
1·979	40	1·990	90
2·009	50	1·984	100

These tables show that, at higher strengths, the density does not enable one to find the concentration of the acid.

On account of its great **affinity for water,** concentrated sulphuric acid is used for drying gases on which it does not act chemically. It is most conveniently spread over pumice by boiling pieces of this substance with the acid ; the lumps of impregnated pumice are placed in a glass tower.

The affinity of strong sulphuric acid for water is also shown by the charring of organic matter containing carbon, hydrogen, and oxygen, by the acid. The elements of water are removed, and black carbon is left.

EXPT. 191.—To a strong syrup of cane-sugar, $C_{12}H_{22}O_{11}$, contained in a beaker standing in a stoneware trough, add concentrated sulphuric acid. The mixture rapidly becomes dark in colour and hot, and froths up into a black mass of finely-divided carbon, clouds of steam and sulphur dioxide being evolved. If the black mass is washed with water on a filter-paper, a dark brown colloidal solution of carbon passes through.

Other organic substances, such as wood, are charred; pure cellulose, such as filter-paper, is not charred by the cold, slightly diluted, acid, but forms a tough, semi-transparent material, known as **parchment-paper,** which since it is impervious to fats is used for wrapping butter and other greasy materials.

By heating concentrated sulphuric acid with benzene, C_6H_6, elimination of water occurs, and **benzenesulphonic acid,** $C_6H_5 \cdot SO_3H$, is produced: $C_6H_6 + H_2SO_4 = C_6H_5 \cdot SO_3H + H_2O$. On fusing the sodium salt of this with caustic soda, the sodium compound of **phenol** or "carbolic acid," C_6H_5OH, is produced:

$$C_6H_5SO_3Na + NaOH = C_6H_5ONa + Na_2SO_3.$$

The sodium phenoxide, C_6H_5ONa, may be decomposed by an acid (even carbon dioxide under pressure), and phenol is formed. Many other sulphonic acids, all containing the group SO_3H—, are prepared and used as intermediate products in the manufacture of dyes, drugs, etc. Very often fuming sulphuric acid is used in **sulphonation.**

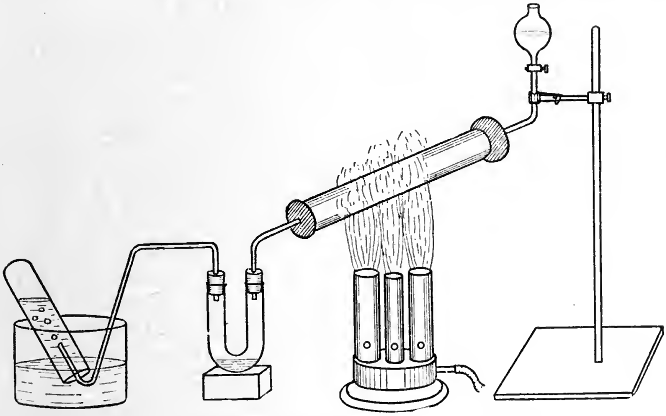


FIG. 279.—Decomposition of Sulphuric Acid by Heat.

The **vapour density** of sulphuric acid at 444° is 25, whilst the calculated density for complete dissociation into SO_3 and H_2O is $(18 + 80)/4 = 24 \cdot 5$. The products recombine on cooling: $H_2SO_4 \rightleftharpoons H_2O + SO_3$. If the vapour is passed through a red-hot tube of platinum or quartz, the sulphur trioxide is decomposed, oxygen and sulphur dioxide being produced: $2H_2SO_4 \rightleftharpoons 2SO_2 + O_2 + H_2O$.

EXPT. 192.—Fit a dropping funnel by means of a mixture of asbestos powder and thick water-glass (sodium silicate) into a silica tube containing broken pumice, and connected with a **U**-tube as shown in Fig. 279. Heat the tube to bright redness by means of powerful Bunsen burners, and allow concentrated sulphuric acid to drop slowly into it. Any undecomposed acid collects in the U-tube, whilst oxygen may be collected in a gas jar over water.

In aqueous solution sulphuric acid behaves as a **strong acid**, since it is largely ionised. The ionisation occurs in two stages, the second being appreciable only at high dilution :

$$H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4{}'$$
$$HSO_4 \rightleftharpoons H^{\cdot} + SO_4{}''.$$

Two series of **sulphates** are therefore known, the **acid** and **normal salts,** corresponding with the formulæ $RHSO_4$ and R_2SO_4. Many of these sulphates are important minerals : *gypsum,* $CaSO_4,2H_2O$; *anhydrite,* $CaSO_4$; *barytes,* $BaSO_4$, *celestine,* $SrSO_4$; *glauberite,* $CaSO_4,Na_2SO_4$; and *kieserite,* $MgSO_4,H_2O$.

Most sulphates are crystalline, and soluble in water. The sulphates of lead, calcium, and strontium are sparingly soluble in water ; barium sulphate is practically insoluble in water and dilute acids, and its formation is used as a **test for sulphuric acid** or soluble sulphates. A solution of barium chloride is added to the liquid to be tested, and then dilute hydrochloric acid. The formation of a white precipitate, $BaSO_4$, indicates the presence of the ion, $SO_4{}''$.

Care should be taken not to add an excess of concentrated hydrochloric acid, as in that case a white precipitate of barium chloride is thrown down, on account of the action of the chloride ion (p. 358). This, however, readily dissolves in water. In the **estimation** of sulphuric acid or sulphates, the boiling solution is mixed with boiling solution of barium chloride. The precipitated $BaSO_4$ is then readily filtered.

Potassium sulphates.—If dilute sulphuric acid is neutralised with caustic potash, or potassium carbonate, and the solution evaporated, anhydrous rhombic prisms of **potassium sulphate,** K_2SO_4, separate. These are not very soluble in water (10·3 gm. in 100 gm. of water at 15° ; 24·1 gm. at 100°) ; the solubility increasing almost linearly with the temperature (Fig. 68). Potassium sulphate melts at 1050°. The salt occurs in large quantities in the double salts of the Stassfurt potash deposits : *schönite,* $K_2SO_4,MgSO_4,6H_2O$; and *kainite,* $K_2SO_4,MgSO_4,MgCl_2,6H_2O$.

If kainite is dissolved in hot water, it breaks up into its constituent salts, which are largely ionised in solution, yielding the ions $K^{\cdot}$,$Mg^{\cdot\cdot}$, $SO_4{}''$,Cl'. By fractional crystallisation, those salts separate first (including double salts) with which the solution first becomes saturated (Van't Hoff). From warm solutions the double salt *schönite* first separates, since it is least soluble, and magnesium chloride remains in solution. If the schönite is digested with potassium chloride (occurring at Stassfurt as *sylvine*), the following reaction occurs: $K_2SO_4,MgSO_4,6H_2O + 2KCl \rightleftharpoons 2K_2SO_4 + MgCl_2 + 6H_2O$. The potassium sulphate, being sparingly soluble, separates first, followed by *carnallite*, $KCl,MgCl_2,6H_2O$, from which KCl and $MgCl_2$ can be prepared (p. 791).

Potassium sulphate is also obtained in smaller amounts by the action of concentrated sulphuric acid on the chloride: $2KCl + H_2SO_4 = K_2SO_4 + 2HCl$; and as a by-product in the manufacture of potassium dichromate (p. 947) and permanganate (p. 966). Potassium sulphate is used in the preparation of potash alum (p. 899) and as a fertiliser (p. 789).

If potassium sulphate is heated with an equivalent of concentrated sulphuric acid, it dissolves; **potassium hydrogen sulphate** ("potassium bisulphate," $K_2O,2SO_3$, or "acid potassium sulphate"), $KHSO_4$, being formed, which fuses at 197° (Roulle, 1754). This is obtained as a by-product in the preparation of nitric acid (p. 566). It is readily soluble in water; the solution giving a strongly acid reaction, owing to the formation of hydrogen ions:

$$KHSO_4 \rightleftharpoons K^{\cdot} + HSO_4'$$
$$HSO_4' \rightleftharpoons H^{\cdot} + SO_4''.$$

On evaporation, this solution, in accordance with Van't Hoff's rule, deposits the normal sulphate, K_2SO_4, which is the salt with which the solution first becomes saturated. The residual solution contains free sulphuric acid. From this, on cooling, a **trisulphate,** $K_2SO_4,KHSO_4$, or $K_2O,3SO_3,H_2O$, deposits, and finally $KHSO_4$. The compounds $K_2SO_4,3KHSO_4$ and $K_2SO_4,6KHSO_4$ are known.

At a red heat, potassium hydrogen sulphate loses water and forms **potassium pyrosulphate:** $2KHSO_4 = H_2O + K_2S_2O_7$. At higher temperatures this evolves sulphur trioxide: $K_2S_2O_7 = K_2SO_4 + SO_3$; hence it is used to attack refractory minerals in analysis, since it behaves like sulphuric acid of high boiling point. Thus chromite, FeO,Cr_2O_3, is converted into ferrous and chromic sulphates, $FeSO_4$ and $Cr_2(SO_4)_3$, although it is not attacked by boiling sulphuric acid.

Sodium sulphates.—Normal sodium sulphate, Na_2SO_4, is prepared in large quantities as *salt-cake* in the first part of the Leblanc process (p. 777). It crystallises from water as *Glauber's salt,* $Na_2SO_4,10H_2O$, forming large monoclinic prisms, which effloresce readily in the air, and fall to a white powder of anhydrous salt: $Na_2SO_4,10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$ (vap.). The crystals melt at 32·48°, but deposition of anhydrous salt simultaneously occurs. The solubility of Glauber's salt is peculiar, since it reaches a maximum at 32·48° (Fig. 68). At this temperature the solid in contact with the solution is converted into the anhydrous salt, the solubility of which diminishes with further rise of temperature. The solubility curve therefore consists of two parts, meeting in a sharp angle at

32·48°, the first part being the solubility curve of Glauber's salt, and the second part that of anhydrous sodium sulphate.

Glauber's salt readily shows the phenomenon of supersaturation (p. 101). If the supersaturated solution is brought in contact with a minute crystal of Glauber's salt, such as one of those which are always floating in dusty air, crystallisation at once begins, and Glauber's salt is deposited. But if it is cooled to 5°, it deposits crystals of a metastable heptahydrate, $Na_2SO_4,7H_2O$, which become opaque when touched with a crystal of Glauber's salt, owing to decomposition :

$$2Na_2SO_4,7H_2O = Na_2SO_4,10H_2O + Na_2SO_4 + 4H_2O.$$

The anhydrous sulphate occurs as *thenardite*; *glauberite* is the double salt $CaSO_4,Na_2SO_4$.

Sodium hydrogen sulphate, $NaHSO_4$ ("sodium bisulphate"), is formed in large triclinic prisms by the action of warm concentrated sulphuric acid on anhydrous sodium sulphate. It is formed in the preparation of hydrochloric acid (p. 229). A fused mixture, or compound, of this salt and the normal sulphate is formed as a by-product in the manufacture of nitric acid (p. 573), and is known as *nitre-cake*. The salts $NaHSO_4,H_2O$ and $Na_2SO_4,NaHSO_4$ are known. The acid sulphate of sodium is decomposed by alcohol into the salt $NaHSO_4,Na_2SO_4$, and free sulphuric acid: $3NaHSO_4 \rightleftharpoons Na_2SO_4,NaHSO_4 + H_2SO_4$. Dry $KHSO_4$ is not decomposed by dry alcohol. **Sodium pyrosulphate,** $Na_2S_2O_7$, is formed on gentle ignition of the acid sulphate, or by the action of sulphur trioxide on common salt : $2NaCl + 3SO_3 = Na_2S_2O_7 + SO_2Cl_2$. On heating to redness, it decomposes into sulphur trioxide and the normal sulphate. The solution of sodium hydrogen sulphate is acid, for the same reason as that of the potassium salt, but on evaporation above 50° it yields crystals of $NaHSO_4$.

The chlorides of sulphuric acid.—If sulphuric acid is treated with phosphorus pentachloride, PCl_5, hydrogen chloride is evolved, and two compounds are formed which have the formulæ SO_3HCl and SO_2Cl_2. The reaction involves the replacement of one or two OH groups, respectively, by Cl, and is similar to the action of the phosphorus halides on water (p. 640). Since it has been found that this reaction always occurs when hydroxyl groups are present in a compound, it is assumed that sulphuric acid has the formula $SO_2(OH)_2$, the radical $SO_2\Big<$ being called **sulphuryl.** The interaction of the phosphorus pentachloride is then represented by the equations :

$$SO_2(OH)_2 + PCl_5 = SO_2(OH)Cl + POCl_3 + HCl$$
$$SO_2(OH)Cl + PCl_5 = SO_2Cl_2 + POCl_3 + HCl.$$

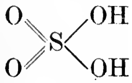
The three substances may be separated by fractional distillation, since their boiling points are quite different; $POCl_3$, 107·2°; $SO_2(OH)Cl$, 155·3°; SO_2Cl_2, 69°.

The compounds $SO_2(OH)Cl$ and SO_2Cl_2 are known as **chlorides of sulphuric acid**; they belong to the general class of **acid chlorides**, which are formed by the exchange of hydroxyl groups for chlorine, and with water are reconverted into the original acids:

$$SO_2(OH)Cl + H_2O = SO_2(OH)_2 + HCl$$
$$SO_2Cl_2 + 2H_2O = SO_2(OH)_2 + 2HCl.$$

The two compounds $SO_2(OH)Cl$ and SO_2Cl_2, known as **chlorosulphonic acid** and **sulphuryl chloride**, respectively, both contain the bivalent radical sulphuryl; the former, if written as SO_3HCl, is seen to contain the characteristic grouping, SO_3H, of sulphonic acids, hence its name.

Since sulphuric acid contains two hydroxyl groups, the radical SO_2 must be bivalent; the two oxygen atoms of this radical are united by two valencies each to the sulphur atom, and the latter must therefore be sexivalent. The graphic formula of sulphuric acid is therefore:

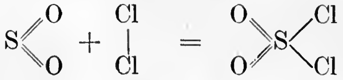


Chlorosulphonic acid, SO_3HCl, may be obtained by the direct combination of sulphur trioxide and hydrogen chloride: $SO_3 + HCl = SO_3HCl$, or by the action of phosphorus pentachloride on sulphuric acid as explained above. Since an excess of the phosphorus pentachloride produces sulphuryl chloride, phosphorus oxychloride, $POCl_3$, may be used instead, as this does not interact further with chlorosulphonic acid: $2SO_2(OH)_2 + POCl_3 = 2SO_2(OH)Cl + HPO_3 + HCl$. It is obtained on the large scale by passing dry hydrogen chloride through fuming sulphuric acid (containing SO_3), and distilling. Chlorosulphonic acid is a colourless, fuming liquid, sp. gr. 1·776, which is violently decomposed by water, producing sulphuric and hydrochloric acids. When heated to 170–190° it decomposes into SO_2Cl_2 and H_2SO_4; at higher temperatures it breaks down into Cl_2, SO_2, and H_2O. It reacts violently with silver nitrate, forming nitrososulphuric acid:

$$2SO_3HCl + 2AgNO_3 = 2AgCl + 2SO_2(OH)O{\cdot}NO + O_2.$$

Sulphuryl chloride, SO_2Cl_2, is produced by the direct combination of chlorine and sulphur dioxide in presence of sunlight, or under the catalytic influence of camphor, glacial acetic acid, or animal charcoal: $SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$. It is formed by the prolonged action of phosphorus pentachloride on sulphuric acid, or by heating chlorosulphonic acid in a sealed tube at 180°. It may be produced by a modification of the last reaction, by heating a mixture of chlorosulphonic acid with 1 per cent. of mercuric sulphate, which acts as a catalyst, in a flask under a reflux condenser heated to 70°, and condensing the vapour.

Sulphuryl chloride is a colourless, fuming liquid which boils at 69° without decomposition. It is rapidly decomposed by water, with formation of sulphuric and hydrochloric acids; chlorosulphonic acid is formed as an intermediate stage. With ice-cold water it forms a crystalline hydrate, $SO_2Cl_2,15H_2O$. The direct formation of SO_2Cl_2 from SO_2 and Cl_2 shows that its graphic formula contains a sexivalent sulphur atom, since chlorine always adds on to sulphur in preference to oxygen:



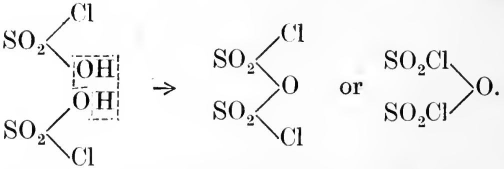
The chloride of pyrosulphuric acid, **pyrosulphuryl chloride,** $S_2O_5Cl_2$, is obtained by the action of sulphur trioxide on sulphuryl chloride or on sulphur chloride:

$$SO_2Cl_2 + SO_3 = S_2O_5Cl_2$$
$$5SO_3 + S_2Cl_2 = 5SO_2 + S_2O_5Cl_2.$$

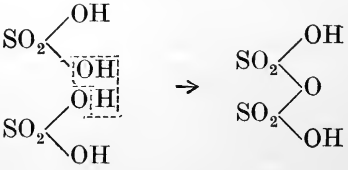
It is also formed by the action of sulphur trioxide or chlorosulphonic acid on phosphorus pentachloride:

$$2SO_3 + PCl_5 = POCl_3 + S_2O_5Cl_2$$
$$2SO_2(OH)Cl + PCl_5 = POCl_3 + 2HCl + S_2O_5Cl_2.$$

It is a heavy, mobile liquid, sp. gr. 1·844/18°, boiling at 150·7° under 730 mm. pressure, giving a normal vapour density. It fumes only slightly and is decomposed only *slowly* by water: $S_2O_5Cl_2 + 3H_2O = 2H_2SO_4 + 2HCl$. It may be regarded as produced from 2 molecules of chlorosulphonic acid by elimination of water:



In the same way, pyrosulphuric acid, $H_2S_2O_7$, may be regarded as formed from 2 molecules of sulphuric acid by the elimination of a molecule of water:



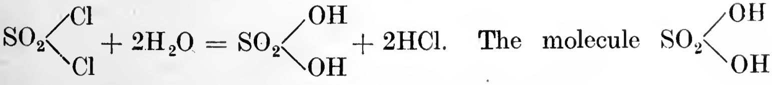
Such reactions, in which certain atoms are removed from *two* or more molecules, and the residues combine to form a single molecule, are called **condensations.**

The compounds $SO_2(OH)F$ (b.-pt. 162·6°), obtained by heating fluorspar with fuming sulphuric acid, SO_2F_2 (b.-pt. $-52°$), and solid $S_2O_3Cl_4 (SO_3HCl + SCl_4 = S_2O_3Cl_4 + HCl)$, are known.

Negative groups.—Although all **acids** contain hydrogen which can be ionised in solution, there are numerous hydrogen compounds, such as NH_3 and NaH, which have no acidic properties. One atom of hydrogen in ammonia, NH_3, can be replaced by the metals sodium, potassium, or lithium, forming sodamide, $NaNH_2$, etc. Hydrogen atoms in hydrocarbons may also, by indirect means, be replaced by metals, forming **organo-metallic compounds;** thus, from ethane, C_2H_6, we can obtain zinc ethyl, $Zn(C_2H_5)_2$. It is therefore not sufficient that a substance shall contain hydrogen which can be replaced by metals in order that it shall be an acid. Acidic hydrogen, however, is always replaced, appearing in the form of water, by metals presented to it in the form of hydroxides, and this statement is equivalent to saying that acidic hydrogen is that which can form hydrogen ions, the latter uniting with hydroxyl to form water (p. 294) : $H^{\cdot} + OH' \rightleftarrows H_2O$.

The acidic character of certain hydrogen compounds is determined by the character of the rest of the molecule of these compounds. In the hydracids of halogens, for instance, the hydrogen is united with a *strongly electronegative atom* of halogen, and strong acids result. In H_2S the hydrogen is united with the weakly electronegative atom of sulphur, and H_2S is a very weak acid. The case of water, H_2O, is exceptional, since it combines both acid and basic functions, ionising into $H^{\cdot}$ and OH'.

In the **oxy-acids,** *the acidic hydrogen is directly linked to oxygen as hydroxyl,* OH, which, of course, is not usually ionisable as the hydroxide ion. Thus, the action of water on sulphuryl chloride gives sulphuric acid, showing that Cl in the SO_2Cl_2 is replaced by OH :



$SO_2{<}^{Cl}_{Cl} + 2H_2O = SO_2{<}^{OH}_{OH} + 2HCl$. The molecule $SO_2{<}^{OH}_{OH}$ may therefore be regarded as formed by the replacement of 2 atoms of hydrogen from 2 molecules of water by the bivalent negative radical sulphuryl : $=SO_2$. This constitution, first deduced by Williamson (1852), is expressed by saying that sulphuric acid and other oxy-acids are built up on the **water-type.**

The acidic character of the hydrogen in oxy-acids is therefore due to the presence of a **negative group,** *e.g.*, $>SO_2$, in the molecule.

In organic acids this negative group is uniformly the **carbonyl group,** $>CO$. Thus, acetic acid is $CH_3{\cdot}CO{\cdot}OH$, and oxalic acid is $(CO{\cdot}OH)_2$.

If hydroxyl is combined with a **positive group,** such as an atom of metal, or a radical such as ammonium, NH_4, it ionises as such, and the compound shows **basic properties.** The more strongly electropositive is the metal, or radical, the stronger is the base. Thus, KOH is a strong base, $Fe(OH)_3$ is a weak base.

If the positive group is only weakly electropositive, the compound may show weakly acidic properties. Thus, $Al(OH)_3$ behaves either as a weak base or as a weak acid, according as it is treated with a strong acid or a strong base (p. 360) : $Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$; $Al(OH)_3 + KOH = KAlO_2 + 2H_2O$. The organic amino-acetic acid, containing both the positive amino-group,—NH_2, and the negative carbonyl group $>CO$, is at the same time a weak base and a weak acid : $CH_2{\cdot}NH_2{\cdot}CO{\cdot}OH$. Such a substance is called **amphoteric ;** the acidic and basic properties are then very weak and practically evenly balanced.

Persulphuric Acids.

Persulphuric acids.—Faraday (1832), when electrolysing an aqueous solution of sulphuric acid, observed that, if the acid were concentrated, "a remarkable disappearance of oxygen took place." In 1878 Berthelot exposed a mixture of sulphur dioxide and oxygen to the silent discharge, and obtained a contraction corresponding with the formation of S_2O_7. A small quantity of viscous liquid separated on the walls of the ozoniser, which solidified at 0° to long prismatic crystals. This was supposed by Berthelot to be **persulphuric anhydride,** S_2O_7. Marshall (1891) found that if a concentrated solution of potassium hydrogen sulphate, $KHSO_4$, is electrolysed, crystals of the composition KSO_4 separate at the anode.

In Faraday's experiment **persulphuric acid** is formed, probably from the ions HSO_4' discharged at the anode : $H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4'$; $2HSO_4 = H_2S_2O_8$. The doubled formula is confirmed by the determination of the molecular weight of the potassium salt by the freezing-point method ; this is found to be $K_2S_2O_8$.

Expt. 193.—Persulphuric acid is readily formed by the electrolysis of 50 per cent. sulphuric acid with an anode formed of a fine platinum point, surrounded by a glass tube to serve as a diaphragm. The cathode consists of a ring of platinum wire placed outside the diaphragm (Fig. 280). The apparatus is kept cool by immersion in a freezing mixture.

If potassium hydrogen sulphate solution is used in the same apparatus, crystals of the persulphate separate out. As strong a solution as possible should be used. The solution in each experiment gives a brown colour with potassium iodide: $H_2S_2O_8 + 2KI = 2KHSO_4 + I_2$.

In the preparation of potassium persulphate, the ions, HSO_4', crowding together at the anode are discharged, and persulphuric acid is formed: $2HSO_4 = H_2S_2O_8$. This reacts with the potassium hydrogen sulphate, and the sparingly soluble persulphate crystallises out: $H_2S_2O_8 + 2KHSO_4 \rightleftharpoons K_2S_2O_8 + 2H_2SO_4$.

A solution of a persulphate acts as a powerful oxidising agent. Besides slowly liberating iodine from iodides, it oxidises manganous salts to manganese dioxide, precipitates red copper peroxide, CuO_2, from solutions of copper salts, and black silver peroxide from silver nitrate. The ammonium salt, $(NH_4)_2S_2O_8$, prepared in the same way as the potassium salt, is the most soluble persulphate; it is used for bleaching, and in photography to "reduce" the intensity of negatives. The barium salt is very soluble in water, and serves to separate persulphuric acid from sulphuric acid.

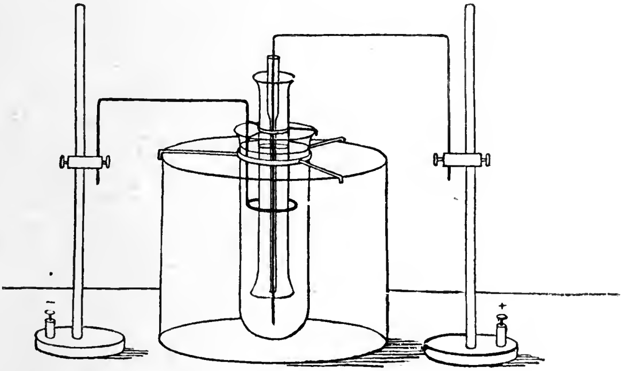


FIG. 280.—Preparation of Persulphuric Acid.

Caro in 1898, by dissolving potassium persulphate in concentrated sulphuric acid, obtained a solution of a new persulphuric acid, which was a powerful oxidising agent, converting aniline into nitrobenzene, but differing from Marshall's acid. This acid, known as **Caro's acid,** was investigated by Baeyer and Villiger in 1901. They prepared it by grinding $K_2S_2O_8$ with concentrated sulphuric acid, allowing to stand one hour, and pouring on to ice. Sulphuric acid was removed by shaking with the sparingly soluble barium phosphate. The solution might contain Marshall's acid, Caro's acid, and hydrogen peroxide. These three substances were differentiated by the following reactions :

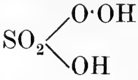
1. Caro's acid liberates iodine from potassium iodide instantly.
2. Marshall's acid liberates iodine from iodides only slowly.
3. Hydrogen peroxide at once reduces potassium permanganate, whilst this is not changed by persulphuric acids.

In the solution they determined the ratio SO_3 : peroxide O, and found this to be 1 : 1; hence the formula of Caro's acid is $SO_3 + O + H_2O$, or H_2SO_5. The free acid was prepared in a pure state by Ahrle (1909) by the action of sulphur trioxide on anhydrous hydrogen peroxide : $SO_3 + H_2O_2 = H_2SO_5$. The reaction with concentrated sulphuric acid is reversible : $H_2SO_4 + H_2O_2 \rightleftharpoons H_2SO_5 + H_2O$. Caro's acid is crystalline, melts at 45°, and is stable for some days. D'Ans and Friedrich (1910) prepared both Caro's acid and Marshall's acid by the action of hydrogen peroxide on chlorosulphonic acid :

$$HO{\cdot}SO_2{\cdot}Cl + H_2O_2 = HO{\cdot}SO_2{\cdot}O{\cdot}OH + HCl$$
$$HO{\cdot}SO_2{\cdot}Cl + HO{\cdot}SO_2{\cdot}O{\cdot}OH = HO{\cdot}SO_2{\cdot}O{\cdot}O{\cdot}SO_2{\cdot}OH + HCl.$$

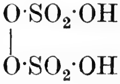
$H_2S_2O_8$ forms crystals stable up to 60°, but in solution slowly passes into Caro's acid and sulphuric acid : $H_2O + H_2S_2O_8 = H_2SO_4 + H_2SO_5$.

The constitution of Caro's acid, or **permonosulphuric acid,** is seen by the above reactions to be



$$SO_2\begin{cases}O{\cdot}OH\\OH\end{cases};$$

whilst that of **perdisulphuric acid,** or the ordinary acid, is :



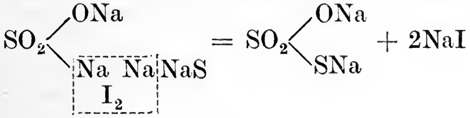
$$\begin{array}{l}O{\cdot}SO_2{\cdot}OH\\|\\O{\cdot}SO_2{\cdot}OH\end{array}$$

These formulæ agree with the constitution adopted for hydrogen peroxide.

THIOSULPHURIC AND THIONIC ACIDS.

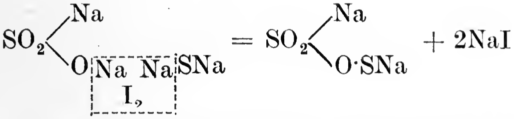
Thiosulphuric acid.—If a solution of sodium sulphite is boiled with flowers of sulphur, a salt separates on evaporation and cooling which has the formula $Na_2S_2O_3,5H_2O$. This may be regarded as sodium sulphate in which an atom of oxygen is replaced by one of sulphur, and is hence known as **sodium thiosulphate.** It is commonly called sodium "hyposulphite," but this name is more appropriately given to the compound $Na_2S_2O_4$ (p. 525). On account of the similarity in the chemical properties of oxygen and sulphur, one may suppose that the sulphur atom in the above reaction : $Na_2SO_3 + S = Na_2S_2O_3$, enters the molecule of the sulphite in the same position as the oxygen atom in the reaction $Na_2SO_3 + O = Na_2SO_4$. The formula of sodium sulphite, however, may be either $SO_2\left\langle\begin{matrix}ONa\\Na\end{matrix}\right.$ or $SO\left\langle\begin{matrix}ONa\\ONa\end{matrix}\right.$ (p. 496), so that there are two possible formulæ for the thiosulphate, viz., $SO_2\left\langle\begin{matrix}ONa\\SNa\end{matrix}\right.$ or $SO{\cdot}S\left\langle\begin{matrix}ONa\\ONa\end{matrix}\right.$. Spring, by the action of iodine on a mixture of sodium sulphide and sodium sulphite, obtained sodium thiosulphate. This is a condensation reaction, and two modes of interaction are possible :

I.



$$SO_2\left\langle\begin{matrix}ONa\\ \boxed{\begin{matrix}Na\ Na\\ I_2\end{matrix}}NaS\end{matrix}\right. = SO_2\left\langle\begin{matrix}ONa\\SNa\end{matrix}\right. + 2NaI$$

II.



$$SO_2\left\langle\begin{matrix}Na\\ O\boxed{\begin{matrix}Na\ Na\\ I_2\end{matrix}}SNa\end{matrix}\right. = SO_2\left\langle\begin{matrix}Na\\O{\cdot}SNa\end{matrix}\right. + 2NaI$$

It is considered that I. is more probable, since the formula of the thiosulphate is then more analogous to that of the sulphate. Spring showed that if the thiosulphate is treated with sodium amalgam and water, the above condensation reaction is reversed, and sodium sulphite and sodium sulphide are produced. Further, if sodium silver thiosulphate, produced when a silver salt is dissolved in a solution of sodium thiosulphate (p. 828), is boiled with water, a black precipitate of silver sulphide is produced : $SO_2(OAg)(SAg) + H_2O = SO_2(OH)_2 + Ag_2S$.

Sodium thiosulphate, $Na_2S_2O_3,5H_2O$, commonly called "hypo," is made by boiling the sulphite with sulphur, or by oxidising **alkali-waste,** containing calcium disulphide, CaS_2, by exposure to air and then precipitating the calcium with sodium carbonate :

$$2CaS_2 + 3O_2 = 2CaS_2O_3, \quad \text{and} \quad CaS_2O_3 + Na_2CO_3 = CaCO_3 + Na_2S_2O_3.$$

If sulphur is boiled (or fused) with a caustic alkali, or milk of lime, a thiosulphate is produced as well as a sulphide : $6NaOH + 4S = Na_2S_2O_3 + 2Na_2S + 3H_2O$. Thiosulphates are also formed by passing sulphur dioxide through solutions of sulphides : the reaction (which led to the discovery of thiosulphates by Chaussier in 1799), according to Vauquelin probably proceeds in three stages :

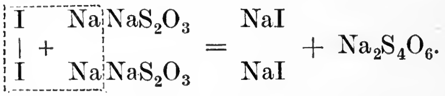
1. $SO_2 + Na_2S + H_2O = Na_2SO_3 + H_2S$.
2. $SO_2 + 2H_2S = 2H_2O + 3S$.
3. $Na_2SO_3 + S = Na_2S_2O_3$.

If a solution of sodium thiosulphate is acidified, free **thiosulphuric acid,** $H_2S_2O_3$ (which is unknown), is probably first formed, but immediately decomposes into sulphurous acid and free sulphur, which slowly deposits as a white turbidity: $H_2S_2O_3 = H_2SO_3 + S$. The delay in the appearance of the precipitate is due to the formation of a colloidal solution, and not to the slow decomposition of $H_2S_2O_3$, since the sulphur is ultimately precipitated, even if the solution, after acidification, is at once neutralised with caustic soda, when any $H_2S_2O_3$ would be reconverted into $Na_2S_2O_3$.

Sodium thiosulphate readily dissolves silver chloride, bromide, and iodide, forming double salts, which have a sweet taste, *e.g.*, $NaAgS_2O_3$. For this reason the salt is used in photography to remove unaltered silver halides from the negatives or prints, so as to render these permanent to light (" fixing," p. 830).

It is very readily oxidised by chlorine water: $Na_2S_2O_3 + 4HOCl + H_2O = Na_2SO_4 + H_2SO_4 + 4HCl$, and is used as an **antichlor** to remove traces of chlorine from bleached fabrics. With bromine the reaction is similar, but with iodine an entirely different reaction occurs.

Tetrathionic acid, $H_2S_4O_6$.—If a solution of sodium thiosulphate is added to a solution of iodine, the colour of the latter is discharged. This is used in the titration of iodine; a little starch-paste may be added when the colour is almost discharged, and the blue colour then disappears when the last trace of iodine has reacted. The product of the reaction is not sodium sulphate, but a new salt of the formula $Na_2S_4O_6$, **sodium tetrathionate;** it was discovered by Fordos and Gélis in 1843. The reaction is: $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$. It is one of **condensation**:



$$\begin{array}{ll} \text{I} & \text{Na}\,\text{NaS}_2\text{O}_3 \\ | + & \\ \text{I} & \text{Na}\,\text{NaS}_2\text{O}_3 \end{array} = \begin{array}{l} \text{NaI} \\ \\ \text{NaI} \end{array} + \text{Na}_2\text{S}_4\text{O}_6.$$

The reaction is quantitative. To obtain the pure salt, a saturated aqueous solution of sodium thiosulphate is added drop by drop to a cooled solution of iodine in alcohol. The tetrathionate separates as it is formed; it is washed with alcohol, dissolved in water, reprecipated with alcohol, and dried over sulphuric acid. In solution the salt slowly decomposes: $Na_2S_4O_6 = Na_2SO_4 + SO_2 + 2S$; the reaction is accelerated by sodium thiosulphate.

If lead acetate is added to a solution of sodium thiosulphate, a white precipitate of lead thiosulphate is obtained. This, when suspended in water and treated with iodine, gives a solution of lead tetrathionate: $2PbS_2O_3 + I_2 = PbI_2 + PbS_4O_6$. When this is precipitated with sulphuretted hydrogen, a solution of free **tetrathionic acid,** $H_2S_4O_6$, is obtained. The solution may be concentrated on a water-bath, and is fairly stable. When concentrated beyond a certain point, however, it decomposes: $H_2S_4O_6 = H_2SO_4 + SO_2 + 2S$.

By the action of sodium amalgam and water on sodium tetrathionate, the reaction of condensation by which it was formed is reversed, and sodium thiosulphate is reproduced: $Na_2S_4O_6 + 2Na = 2Na_2S_2O_6$.

Tetrathionates give with sulphides a precipitate of sulphur: $Na_2S_4O_6 + Na_2S = 2Na_2S_2O_3 + S$.

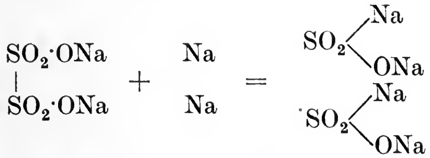
Dithionic acid.—If finely-ground pyrolusite (native crystalline manganese dioxide) is suspended in water and sulphur dioxide passed in, manganous sulphate is formed, together with the salt of a new acid (Gay-Lussac and Welter, 1819). If the liquid, after several hours' treatment, is filtered and baryta water added, a precipitate of barium sulphate is formed, and the barium salt of the new acid remains in solution. On evaporation colourless crystals of **barium dithionate,** $BaS_2O_6,2H_2O$, separate.

Manganic sulphite is first formed, and then decomposes as follows:

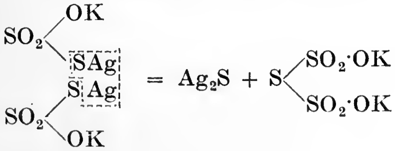
$$2MnO_2 + 3H_2SO_3 = Mn_2(SO_3)_3 + 3H_2O + O.$$
$$Mn_2(SO_3)_3 = MnS_2O_6 + MnSO_3.$$
$$MnSO_3 + O = MnSO_4.$$
$$MnS_2O_6 + Ba(OH)_2 = Mn(OH)_2 + BaS_2O_6.$$

By decomposing the barium salt with the calculated amount of sulphuric acid, a solution of **dithionic acid,** $H_2S_2O_6$, is formed, which may be concentrated on a water-bath to a certain extent, but then decomposes: $H_2S_2O_6 = H_2SO_4 + SO_2$. No sulphur is deposited. The salts decompose on heating in a similar manner: $K_2S_2O_6 = K_2SO_4 + SO_2$.

On treating sodium dithionate with sodium amalgam, sodium sulphite is formed, hence the formula of the acid is probably $(SO_2 \cdot OH)_2$:



Trithionic acid.—By the action of heat on a solution of *potassium* silver thiosulphate, silver sulphide is precipitated, and the solution contains the sodium salt of **trithionic acid,** $Na_2S_3O_3$:



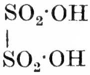
The same salt is formed by saturating a solution of potassium thiosulphate with sulphur dioxide until it is yellow, allowing it to stand till colourless, and again passing in SO_2: $3SO_2 + 2K_2S_2O_3 = 2K_2S_3O_6 + S$. The salt crystallises out.

Pentathionic acid.—If sulphuretted hydrogen is passed into a solution of sulphurous acid, a variety of substances is formed. Colloidal sulphur is precipitated, and the milky liquid, known as **Wackenroder's solution** (1845), contains two new thionic acids, **pentathionic acid,** $H_2S_5O_6$, and **hexathionic acid,** $H_2S_6O_6$. If it is treated with one-third of an equivalent of caustic potash and allowed to evaporate spontaneously, a mixture of tetrathionate and pentathionate is obtained, which may be separated by recrystallisation from warm water. The mother liquor on spontaneous evaporation deposits a crust of a salt richer in sulphur, probably the hexathionate. The crystals of tetrathionate and pentathionate may also be separated by flotation in a mixture of xylene and bromoform ($CHBr_3$), of sp. gr. 2·2. $K_2S_4O_6$ sinks, whilst $K_2S_5O_6$ rises (*cf.* p. 9). The solution contains, in addition to these two thionic acids, sulphuric acid and a trace of trithionic acid.

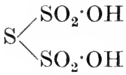
The reactions leading to formation of Wackenroder's solution have been represented as follows by Debus (1888):

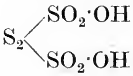
I. $H_2S + 3SO_2 = H_2S_4O_6$.
II. $H_2S_4O_6 + H_2SO_3 = H_2S_3O_6 + H_2S_2O_3$.
III. $2H_2S_3O_6 + 5H_2S = H_2SO_4 + H_2S_2O_3 + 5H_2O + 8S$.
IV. $H_2S_4O_6 + H_2S_2O_3 = H_2S_5O_6 + H_2SO_3$.

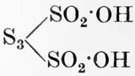
The **constitution of the thionic acids** has been indicated above. The formulæ at present accepted are those proposed by Mendeléeff and Blomstrand (1870):



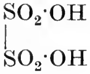
$$\begin{array}{c}SO_2{\cdot}OH\\ |\\ SO_2{\cdot}OH\end{array}$$



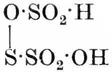




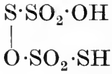
The alternative formulæ proposed by Debus are considered less probable, although the evidence for each set of formulæ is not too convincing:



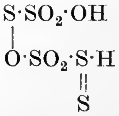
$$\begin{array}{c}SO_2{\cdot}OH\\ |\\ SO_2{\cdot}OH\end{array}$$



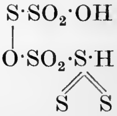
$$\begin{array}{l}O{\cdot}SO_2{\cdot}H\\ |\\ S{\cdot}SO_2{\cdot}OH\end{array}$$



$$\begin{array}{l}S{\cdot}SO_2{\cdot}OH\\ |\\ O{\cdot}SO_2{\cdot}SH\end{array}$$



$$\begin{array}{l}S{\cdot}SO_2{\cdot}OH\\ |\\ O{\cdot}SO_2{\cdot}S{\cdot}H\\ \qquad\qquad \|\\ \qquad\qquad S\end{array}$$



Hertlein (1896) found that the polythionates of mercury and silver do not form complex compounds; hence it is probable that the metal is attached to oxygen, as in Blomstrand and Mendeléeff's formulæ, rather than to sulphur, as in Debus's formulæ, since these metals in combination with sulphur readily form complex compounds (p. 876). Tetrathionic acid, $HO{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}SO_2{\cdot}OH$, also corresponds with persulphuric acid, $HO{\cdot}SO_2{\cdot}O{\cdot}O{\cdot}SO_2{\cdot}OH$, and the tetrathionates form compounds with ammonia, etc., similar to those formed by persulphates; *e.g.*, $ZnS_4O_6,4NH_3$.

Hyposulphurous acid.—If zinc dust is added to a solution of sulphur dioxide in absolute alcohol, no hydrogen is evolved, but a salt of the formula ZnS_2O_4 crystallises out, which may be dried over concentrated sulphuric acid: $Zn + 2SO_2 = ZnS_2O_4$. This is a salt of **hyposulphurous acid,** $H_2S_2O_4$. The solution of the salt is a powerful bleaching agent, and also shows very powerful reducing properties. Thus, it reduces a solution of copper sulphate to a red precipitate of cuprous hydride, Cu_2H_2, and precipitates mercury and silver from their salts. The moist compound rapidly absorbs oxygen from the air, forming a sulphite.

Sodium hyposulphite (sometimes called **hydrosulphite),** $Na_2S_2O_4$, is prepared by treating a solution of sodium hydrogen sulphite, $NaHSO_3$, with zinc dust, in a corked flask. Milk of lime is then added to precipitate the zinc sodium sulphite which is also formed.

$$4NaHSO_3 + Zn = ZnSO_3,Na_2SO_3 + Na_2S_2O_4 + 2H_2O;$$
$$ZnSO_3,Na_2SO_3 + 2Ca(OH)_2 = Zn(OH)_2 + 2CaSO_3 + 2NaOH.$$

The double salt is also precipitated if alcohol is added to the original solution. The filtrate contains the sodium hyposulphite. It is warmed with a concentrated solution of sodium chloride, and allowed to cool, when thin vitreous prisms of $Na_2S_2O_4,2H_2O$ separate. These are washed with aqueous, and then with anhydrous, acetone, and dried over concentrated sulphuric acid, when anhydrous $Na_2S_2O_4$ remains as a white powder, which after drying in a vacuum at 60° is stable. The hydrate very rapidly absorbs oxygen from the air: $Na_2S_2O_4 + O_2 + H_2O = NaHSO_3 + NaHSO_4$.

The sodium bisulphite solution may first be saturated with sulphur dioxide: $2NaHSO_3 + SO_2 + Zn = Na_2S_2O_4 + ZnSO_3 + H_2O$. Sodium hyposulphite is also formed when sulphur dioxide, diluted with nitrogen or under reduced pressure, acts on sodium hydride: $2NaH + 2SO_2 = Na_2S_2O_4 + H_2$. With pure gas, explosions occur.

The free acid is formed as a yellow solution by adding oxalic acid to a solution of the sodium salt. It rapidly oxidises: $2H_2S_2O_4 + O_2 = 2H_2O + 4SO_2$.

The composition of the hyposulphites was determined by Bernthsen, who showed that, for every two atoms of sulphur in the hyposulphite, *one* atom of oxygen is required to convert it into sulphite (which may be effected by an ammoniacal solution of copper sulphate), and *three* atoms to convert it into sulphate (which is effected by a solution of iodine). These results agree with the formula

S_2O_3 for the anhydride (H_2O,S_2O_3), but not with SO, which was formerly accepted ($H_2SO_2 = H_2O,SO$):

$$S_2O_3 + O = 2SO_2 \qquad S_2O_3 + 3O = 2SO_3$$
$$2SO + 2O = 2SO_2 \qquad 2SO + 4O = 2SO_3.$$

Sodium hyposulphite is used to dissolve indigo, a blue colouring matter $C_{16}H_{10}N_2O_2$, which is insoluble in water; a colourless solution of indigo-white, a reduction compound, is formed:

$$Na_2S_2O_4 + 2H_2O = 2NaHSO_3 + 2H \text{ (nascent)}$$
$$C_{16}H_{10}N_2O_2 + 2H = C_{16}H_{12}N_2O_2.$$

If a fabric is soaked in the solution, and exposed to air, oxidation occurs and indigo-blue is deposited in the fibres. A dye of this character is called a **vat-dye**, and several other kinds are used besides indigo, so that sodium hyposulphite is an important salt in colour chemistry.

Sulphoxylic acid, H_2SO_2, is known only in the form of an organic compound with formaldehyde: $H{\cdot}COH{\cdot}NaHSO_2,2H_2O$.

Sulphur sesquioxide.—If flowers of sulphur are added to fused sulphur trioxide at 10°, blue drops are formed, which solidify to malachite-blue crystalline crusts. This substance is **sulphur sesquioxide,** S_2O_3. It slowly decomposes into sulphur and sulphur dioxide: $2S_2O_3 = 3SO_2 + S$. It dissolves in fuming sulphuric acid to form a blue liquid, which is also produced by dissolving sulphur in the fuming acid (Bucholz, 1804). Water decomposes the sesquioxide, with separation of sulphur and formation of sulphuric and thiosulphuric acids. The oxide is not, therefore, the anhydride of hyposulphurous acid, $H_2S_2O_4$, as might be inferred from its formula. The solution of the sesquioxide in fuming sulphuric acid is used in the manufacture of certain dyes (thiopyrin).

EXERCISES ON CHAPTER XXVI

1. Describe carefully what is observed when: (*a*) roll sulphur is heated in a flask to the boiling point; (*b*) concentrated sulphuric acid is heated with copper turnings; (*c*) flowers of sulphur are added to fuming sulphuric acid. What chemical changes are supposed to occur?

2. How is sulphur dioxide made (*a*) in the laboratory; (*b*) on the large scale? What experiments would you perform in order to ascertain the composition of the gas?

3. Describe what happens when charcoal is heated with concentrated sulphuric acid. How would you proceed to separate the gaseous products of the reaction?

4. What salts may be produced from sulphur dioxide and a solution of caustic soda? What happens when these salts are heated?

5. What is the constitution of sulphurous acid? Assuming that sulphur is sexivalent, what will be its structural formula? What salts should be formed (*a*) on neutralising $NaHSO_3$ with KOH, (*b*) on neutralising $KHSO_3$ with NaOH? If the same salt is produced in both cases, what conclusion would you draw as to the formula of sulphurous acid?

6. By what method would you measure the rate of production of sulphuric acid from a solution of sulphurous acid in presence of oxygen ?

7. What is the action of sulphur dioxide on (*a*) ozone ; (*b*) iodine dissolved in water ; (*c*) iodic acid ; (*d*) lead dioxide ; (*e*) sulphuretted hydrogen ? How would you determine the percentage of sulphur dioxide in the residual gas from vitriol chambers ?

8. How is sulphur trioxide prepared, and what are its properties ? What oxides of sulphur exist besides SO_2 and SO_3, and what is the action of water on them ?

9. Describe the manufacture of fuming sulphuric acid by the contact process. What compounds of water and sulphur trioxide exist ?

10. Describe the manufacture of sulphuric acid by the chamber process. What reactions are supposed to occur in the process, and what experiment may be performed to illustrate these reactions ?

11. What experiments would you perform in order to show that sulphuric acid is a dibasic acid ? An acid is sometimes defined as "a hydrogen compound from which the hydrogen can be replaced by metals." Discuss this.

12. How may sodium sulphite be prepared ? Starting with sodium sulphite, how would you prepare : (*a*) sodium metabisulphite ; (*b*) sodium thiosulphate ; (*c*) sodium hyposulphite ; (*d*) sodium tetrathionate ?

13. What is an acid chloride ? How are the chlorides of sulphurous and sulphuric acids prepared, and what light do they throw on the constitutions of the acids ?

14. Describe briefly how you would prepare specimens of : (*a*) barium dithionate ; (*b*) potassium persulphate ; (*c*) potassium pyrosulphate ; (*d*) sodium tetrathionate.

15. What are sulphonic acids ? How, and for what purposes, are they prepared ?

16. What reactions occur when (*a*) dilute sulphuric acid, (*b*) 50 per cent. sulphuric acid, are electrolysed ? How may the substance formed in the second case be obtained in a pure state, and how has its constitutional formula been established ?

17. How are persulphates prepared ? Describe the preparation of the two persulphuric acids, and describe the method of differentiating between them.

18. Give reactions in which sulphur dioxide acts (*a*) as an oxidising agent ; (*b*) as a reducing agent ; (*c*) as an acid anhydride. How is the bleaching action of sulphur dioxide explained ?

CHAPTER XXVII

SELENIUM AND TELLURIUM

Selenium.—A new element analogous to sulphur was discovered in 1817 by Berzelius, in the deposit formed in a sulphuric acid chamber. It was called **selenium,** from the Greek *selene,* the moon, on account of its analogy to tellurium (*q.v.*).

Selenium occurs in some specimens of native sulphur, particularly Japanese. Metallic **selenides** also occur, *e.g.*, *clausthalite,* $PbSe$, also Cu_2Se and Ag_2Se, at Clausthal (Hartz); *onofrite,* $HgSe,4HgS$, in Mexico; and *crookesite,* $(Cu,Tl,Ag)_2Se$, at Skrikerum (Sweden). It is found in many varieties of pyrites (especially Norwegian), and thence finds its way into the flue-dust, and the commercial sulphuric acid. In making salt-cake with this acid, the selenium passes over as the chloride, $SeCl_4$, into the hydrochloric acid, from which the element can be precipitated in the form of a red powder by sulphur dioxide. To prepare selenium from the flue-dust of pyrites burners, it is digested with a solution of potassium cyanide, when **potassium selenocyanide** (*cf.* $KCNS$) is formed: $KCN + Se = KCNSe$. On addition of hydrochloric acid, selenium is precipitated: $KCNSe + HCl = KCl + HCN + Se$. It is purified by evaporating to dryness with nitric acid, when solid **selenium dioxide,** SeO_2, is formed, which can be recrystallised from hot water as **selenious acid,** H_2SeO_3. A solution of this is reduced by sulphur dioxide: $H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4$. The element is precipitated as a red powder.

Selenium may also be extracted from the anode-slimes in copper refining (p. 809), which may contain as much as 96 per cent. of the element, together with tellurium.

Forms of selenium.—Various modifications of selenium are known: according to Saunders (1900) these fall into three main groups:—

1. **Liquid selenium**—an amorphous solid, which may be regarded as a supercooled liquid of great viscosity. This exists as: (*a*) *Vitreous selenium,* obtained as an opaque lustrous mass, **sp. gr. 4·28,** almost black in colour, but giving a red powder, by suddenly cooling melted selenium. It softens at 50°, and if very rapidly heated to 220° it is

liquid, although viscous. At temperatures above 60–80° it changes fairly quickly, into metallic selenium (*q.v.* 3). (*b*) *Colloidal selenium*, obtained as a red solution by mixing dilute aqueous solutions of selenious and sulphurous acids: $SeO_2 + 2H_2SO_3 = Se + 2H_2SO_4$. The solution slowly deposits (*c*) *amorphous* selenium, a red powder, sp. gr. 4·26, also formed by precipitating a solution of selenium in potassium cyanide by hydrochloric acid, or by subliming selenium in a sealed tube. These three varieties dissolve in carbon disulphide.

2. **Crystalline selenium,** produced from 1 (*a*) or 1 (*c*) on standing in contact with carbon disulphide, by adding benzene to a solution of selenium in carbon disulphide, or by the spontaneous evaporation of this solution. Two stable red, monoclinic, crystalline varieties are known, sp. gr. 4·47 (*cf.* sulphur). If heated rapidly the crystals fuse at 200°; partial conversion into metallic selenium has probably occurred, and the unstable melting point of the crystals is probably 170–180° (*cf.* α-sulphur, p. 479).

3. **Metallic selenium** is formed when any other variety is heated at 200–220° for some time. It is a steel-grey mass, sp. gr. 4·80, giving a black powder (red if very fine), and is insoluble in carbon disulphide (about 1 per cent. of soluble selenium is always present).

The boiling point of selenium is 690°; the vapour is dark red, and its density diminishes with rise of temperature, becoming constant (Se_2) above 1400°.

$t°$	Δ (H = 1)
774	101·2
815	95·4
900–1800	78·6 (Se_2 = 78·5)

The molecular weight in solution in phosphorus corresponds with Se_8.

Metallic selenium, which has been heated for some time at 210°, has the remarkable property of possessing an electrical resistance which varies on exposure to light, diminishing with the intensity of illumination (Willoughby Smith, 1873). When the light is cut off, the original conductivity is recovered after a short time. This effect, which is utilised in the **photophone** and other instruments, was attributed by Siemens (1875) to the existence of two forms of metallic selenium, one a good conductor of electricity and formed from the other on exposure to light. These two forms have been isolated. Form A consists of round granular crystals, stable at 140°, and an insulator in the dark. Form B, which is produced when Form A is heated to 200° for some time, or is exposed to light, forms longer crystals, and is a conductor (Marc, 1903, and Ries, 1908). The action is chiefly produced by red rays.

Selenium is used in making red glass, or red enamels and glazes.

Hydrogen selenide, H_2Se.—This gas is formed by heating selenium in a sealed tube with hydrogen: $H_2 + Se \rightleftharpoons H_2Se$. Most of the selenium sublimes in the form of glittering crystals. By heating iron filings with selenium, iron selenide is formed, which gives H_2Se with acids: $FeSe + 2HCl = FeCl_2 + H_2Se$. Hydrogen selenide is a colourless inflammable gas, with a very offensive smell, and a strong action on the mucous membranes. It is soluble in water, giving a feebly acid solution which precipitates selenides of many metals, and oxidises on exposure to air, selenium being precipitated. The density of the gas is 40·7, and it leaves its own volume of hydrogen when decomposed by heated tin; hence its formula is H_2Se. It liquefies at $-42°$, and solidifies at $-64°$.

No perselenides of hydrogen are known.

Halogen compounds of selenium.—Selenium forms two **fluorides,** SeF_4 and SeF_6, and two **chlorides,** Se_2Cl_2 and $SeCl_4$. The **dichloride,** Se_2Cl_2, is formed as a brown liquid by passing chlorine over fused selenium. It is slowly decomposed by water: $2Se_2Cl_2 + 3H_2O = H_2SeO_3 + 3Se + 4HCl$. On heating it decomposes: $2Se_2Cl_2 = 3Se + SeCl_4$. The **tetrachloride** is therefore more stable than Se_2Cl_2 (*cf.* S_2Cl_2 and SCl_4); it is produced as a white solid by treating the dichloride with chlorine, or by heating SeO_2 with PCl_5: $3SeO_2 + 3PCl_5 = 3SeCl_4 + P_2O_5 + POCl_3$. It sublimes without melting, and its vapour is dissociated: $2SeCl_4 \rightleftharpoons Se_2 + 4Cl_2$ (Evans and Ramsay), or $2SeCl_4 \rightleftharpoons Se_2Cl_2 + 3Cl_2$ (Chabrier). It is decomposed by water: $SeCl_4 + 3H_2O = 4HCl + H_2SeO_3$. By the action of $SeCl_4$ on SeO_2, a yellow liquid **oxychloride,** $SeOCl_2$, is formed. Se_2Br_2 and $SeBr_4$ are known, but the iodides appear to be mixtures.

Oxides and oxy-acids of selenium.—Selenium burns in oxygen with a blue flame, producing a crystalline **dioxide,** SeO_2. Indications of the existence of a second solid oxide, Se_3O_4, have been obtained. A trace of a gaseous oxide (? SeO_3) seems to be produced during the combustion of selenium; it possesses a strong odour of horse-radish. A similar smell, due to carbon diselenide, CSe_2, is emitted when selenium is heated on charcoal before the blowpipe.

If SeO_2 is dissolved in hot water, or selenium boiled with nitric acid, colourless prismatic crystals of **selenious acid,** H_2SeO_3, separate on cooling. It is a dibasic acid, forming acid and normal salts, *e.g.*, $KHSeO_3$, K_2SeO_3. Superacid salts are also formed: $KHSO_3,H_2SeO_3$. It is readily reduced (*e.g.*, by organic matter in dust) with deposition of selenium. Potassium permanganate oxidises selenious to selenic acid.

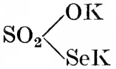
Selenium trioxide is not known, but **selenic acid,** H_2SeO_4, is produced by the action of chlorine on selenium, or selenious acid, suspended in water: $Se + 4H_2O + 3Cl_2 = H_2SeO_4 + 6HCl$; by the action of bromine on silver selenite in water: $Ag_2SeO_3 + H_2O +$

$Br_2 = 2AgBr + H_2SeO_4$; or by the electrolytic oxidation of a solution of selenious acid in nitric acid. The solution may be evaporated until, at 265°, it contains 95 per cent. of H_2SeO_4, which decomposes on further heating. If this liquid is placed over sulphuric acid in an evacuated desiccator until it contains 97·4 per cent. of H_2SeO_4 (sp. gr. 2·627), and is then strongly cooled, crystals of pure selenic acid (m.-pt. 58°) separate. The acid is very hygroscopic and evolves heat when mixed with water; the strong solution chars organic matter. The potassium salt is formed on fusing potassium selenite with nitre (Mitscherlich, 1827), the sodium salt from selenium and sodium peroxide. Selenic acid is also formed by treating SeO_2 with acidified permanganate solution.

The heated acid dissolves copper and gold, producing SeO_2, and selenates. The dilute acid dissolves zinc, iron, etc., liberating hydrogen and forming selenates. Barium selenate is sparingly soluble in water.

Selenic acid is not reduced by sulphur dioxide, or by sulphuretted hydrogen, but it is decomposed, with formation of selenious acid, by boiling with hydrochloric acid, even in dilute solution: $H_2SeO_4 + 2HCl = H_2SeO_3 + Cl_2 + H_2O$. The solution then deposits selenium when treated with sulphur dioxide.

Selenium dissolves in fused sulphur trioxide, or oleum, the compound $SSeO_3$ (**selenosulphur trioxide**) being formed in *green* crystals. (Sulphur gives *blue* S_2O_3; tellurium *bright red* $STeO_3$.)

Selenium dissolves in potassium sulphite solution, giving a pink, unstable solution of the **selenosulphate,**  $SO_2\begin{cases}OK\\SeK\end{cases}$ (*cf.* $K_2S_2O_3$).

Organic compounds of selenium (*e.g.*, selenium indigo) are used in destroying cancer cells.

A very delicate **test for selenium** is the formation of a blue colour with β-imino-α-cyano-hydrindene dissolved in concentrated sulphuric acid: commercial sulphuric acid usually contains sufficient selenium dioxide to give this reaction.

Tellurium.—Tellurium occurs in small quantities in the free state, and was called by the early mineralogists *aurum paradoxum*, or *metallum problematum*, on account of its lustre. Müller von Reichenstein (1782) concluded that it was a peculiar metal; it was more carefully examined by Klaproth (1798), who called it **tellurium.** Berzelius (1832) pointed out its analogies with sulphur and selenium, placing the three elements in the same group. It is now usually regarded as a non-metal.

Tellurium occurs only in relatively small quantities; **native tellurium** is found in Central Europe, America, and Bolivia, but the element more usually occurs in combination with metals as **tellurides**:

graphic tellurium (or *sylvanite*), $(Ag,Au)Te_2$; *black tellurium*, $(Au,Pb)_2(Te,S,Sb)_3$; *hessite*, Ag_2Te; *tetradymite*, Bi_2Te_3, etc. It is present, together with selenium, in Japanese sulphur.

Tellurium is usually extracted from the residues from bismuth ores. These are dissolved in hydrochloric acid, and sodium sulphide is added. Tellurium is precipitated. It is purified by boiling with sodium sulphide solution and powdered sulphur, then adding sodium sulphite: tellurium separates as a greyish-black precipitate, which becomes silver-white on fusion. It crystallises in rhombohedra, is brittle and easily powdered, and has a fairly high sp. gr. of 6·27. It conducts electricity like a metal. An amorphous variety (sp. gr. 6·015) is precipitated by sulphur dioxide from tellurous or telluric acid.

Tellurium melts at 452°, and boils at 1400°; in a nearly perfect vacuum it boils at 478°, forming a golden-yellow vapour. The vapour density at 1400° is slightly higher than that corresponding with Te_2. It burns with a blue flame when heated in air, forming white vapours of **tellurium dioxide,** TeO_2, which is also formed on treating tellurium with nitric acid, or by heating the basic nitrate. TeO_2 occurs native as *tellurite*; it is only sparingly soluble in water, the solution giving no acid reaction with litmus. TeO_2 is in fact also a weak base, forming salts derived from $Te(OH)_4$, *e.g.*, the basic nitrate, $2TeO_2,HNO_3$.

Hydrogen telluride, H_2Te.—This combustible gas was prepared in an impure state by Davy in 1810 by treating zinc telluride with acids; pure H_2Te is obtained from aluminium telluride and dilute hydrochloric acid or by the electrolysis of 50 per cent. sulphuric or phosphoric acid with a tellurium cathode, at once drying the gas, and cooling to $-20°$. It is then obtained as a liquid, b.-pt. 0°, m.-pt. $-48°$. It is fairly stable in the dark, but on exposure to light, especially in presence of moisture, it decomposes: $H_2Te = H_2 + Te$. The vapour density is 65·1, and the volume is unchanged on heating with zinc, hence the formula is H_2Te. By allowing an aqueous solution of H_2Te to oxidise in the air, a claret-red solution of **colloidal tellurium** is formed.

Tellurium, when fused with potassium cyanide, does not form any compound analogous to KCNS or KCNSe, but only K_2Te.

Halogen compounds of tellurium.—**Tellurium dichloride,** $TeCl_2$, is formed as an indistinctly crystalline black mass by passing chlorine over melted tellurium. It gives a deep red vapour, which becomes yellow in air, $TeOCl_2$ and $TeCl_4$ being formed. It is decomposed by water: $2TeCl_2 + 3H_2O = Te + H_2TeO_3 + 4HCl$. With excess of chlorine the *stable* white crystalline **tetrachloride,** $TeCl_4$ (m.-pt. 224°) is formed. This is very hygroscopic, and is hydrolysed by water, producing **tellurous acid,** H_2TeO_3: $TeCl_4 + 3H_2O \rightleftharpoons H_2TeO_3 + 4HCl$. The vapour is stable up to 530°. The **iodide** is formed in iron-grey crystals by the reaction : $H_2TeO_3 + 4HI = TeI_4 + 3H_2O$. TeF_4, TeF_6, $TeBr_2$, $TeBr_4$, are known.

Telluric acid.—**Tellurium trioxide,** TeO_3, is obtained by heating telluric acid, H_2TeO_4. It is an orange-yellow powder, which decomposes when strongly heated : $2TeO_3 = 2TeO_2 + O_2$. It does not recombine with water. **Telluric acid** is a very weak acid, formed by dissolving tellurium in a mixture of nitric and chromic acids, washing the crystals with nitric acid, and recrystallising from water. It forms white crystals of the composition $H_2TeO_4,2H_2O$. These, unlike true crystalline hydrates (*e.g.*, $CuSO_4,5H_2O$), are not permeable to water-vapour in thin plates, hence they appear to have the formula $Te(OH)_6$. The molecular weight in solution also corresponds with this formula. The acid is dimorphous ; below 10° it forms $H_2TeO_4,6H_6O$. It is difficultly soluble in cold water, but readily dissolves in hot water. The methyl ester, $Te(OCH_3)_6$, is also known. When heated to 160°, H_6TeO_6 forms **allotelluric acid,** H_2TeO_4. Metallic **tellurates** are formed by fusing tellurites, *e.g.*, K_2TeO_3, with nitre, or passing chlorine through their alkaline aqueous solutions : $K_2TeO_3 + 2KOH + Cl_2 = K_2TeO_4 + 2KCl + H_2O$. They are not isomorphous with the sulphates, although the acid selenates and tellurates of rubidium are isomorphous. Some tellurates exist in two forms, a colourless salt *soluble* in water and acids, and a yellow *insoluble* form. Normal and acid salts and complex superacid salts (*e.g.*, $K_2TeO_4,Te_3O,4H_2O$; $K_2TeO_4,3TeO_3,4H_2O$) are known. Tellurates are reduced to tellurites on boiling with hydrochloric acid : $K_2TeO_4 + 2HCl = K_2TeO_3 + H_2O + Cl_2$. Barium tellurate is sparingly soluble in water.

If the red compound $STeO_3$ (p. 531) is heated *in vacuo* to 230°, SO_2 is evolved and a brownish-black mass of the **monoxide,** TeO, is left. This dissolves in concentrated sulphuric acid, forming a crystalline mass of **tellurous sulphate,** $Te(SO_4)_2$.

The atomic weight of tellurium.—The anomalous positions of iodine and tellurium in the periodic system led to the suspicion that tellurium might contain an unknown element of higher atomic weight. Brauner (1883) attempted to separate this, and believed that by distilling tellurium in hydrogen its atomic weight was reduced from 127·6 to 125·57. In this case it would correspond with its position in the periodic table.

H. B. Baker and A. H. Bennett (1907) attempted to separate the supposed constituents : (1) by fractional crystallisation of telluric acid ; (2) by boiling barium tellurate with water (the solubility increases in the series $BaSO_4 \rightarrow BaSeO_4 \rightarrow BaTeO_4$) ; (3) by fractional distillation of Te, $Te(C_2H_5)_2$, $TeCl_4$, and TeO_2 ; (4) by fractional electrolysis of tellurium compounds ; (5) by fractional precipitation of $TeCl_4$ with water. The results were all negative. By heating

TeO_2 with sulphur in a small tube (Fig. 281) the reaction $TeO_2 + S = Te + SO_2$ occurred, the excess of sulphur being kept back with silver foil. By this method, and the synthesis of $TeBr_4$, the value **Te = 126·5** (H = 1) was obtained, which is higher than the atomic weight of iodine **I = 125·91**. Flint (1909) claimed to have succeeded in separating tellurium by method (5), but this has not been substantiated by Harcourt and Baker. The value at present accepted is Te = 126·5.

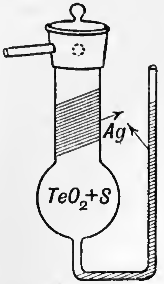


FIG. 281. — Atomic Weight of Tellurium.

EXERCISES ON CHAPTER XXVII

1. From what sources is selenium obtained? Describe the properties of the element. For what purpose is it used?

2. Describe the preparation and properties of the important halogen compounds of selenium and tellurium. Contrast their properties with those of the corresponding compounds of sulphur.

3. How are the oxides and oxy-acids of selenium and tellurium prepared? How do they resemble, or differ from, those of sulphur?

4. Discuss the question of the relative atomic weights of iodine and tellurium from the point of view of the Periodic Law. How has the atomic weight of tellurium been determined?

5. Describe the preparation and properties of the hydrogen compounds of selenium and tellurium. How have their formulæ been established?

CHAPTER XXVIII

NITROGEN AND ITS COMPOUNDS WITH HYDROGEN

Nitrogen.—Scheele (1772) first clearly recognised that air is a mixture of two gases, one of which (*fire air*) supports combustion and respiration, whilst the other (*foul air*) does not. Lavoisier's (1775–6) experiment (p. 47) furnished a decisive proof of this result, although both gases had been separately prepared by Scheele. The latter also showed that, when they were mixed in proper proportions, common air was formed. Lavoisier gave to Scheele's foul air the name **azote** (Greek *a*, no ; *zoe*, life), which is still used in France ; the name **nitrogen** (Greek *nitron*, nitre), suggested by Chaptal, is now used elsewhere for the gas.

In 1772 Daniel Rutherford allowed mice to breathe in air under a bell-jar, and removed the fixed air by washing the residual gas with potash. A gas remained, which he called *mephitic air,* since it did not support combustion or respiration ; unlike fixed air, it was not absorbed by alkali or lime-water. Priestley (1772) burnt charcoal in a confined volume of air, and absorbed the fixed air with alkali, also obtaining mephitic air, which he called *phlogisticated air.* Both these experimenters considered that the gas was common air saturated with phlogiston, or phlogistic material, emitted by the animal or combustible body.

Atmospheric nitrogen was considered to be a pure substance until 1894, when Rayleigh and Ramsay found that it contained a little more than 1 per cent. by weight of an inert gas which, unlike nitrogen, did not combine with heated magnesium. The existence of this gas had been suspected by Cavendish in 1785. The inert gas was called **argon** (Greek *argon*, sluggish) ; later experiments (p. 603) showed that it contained, besides argon, traces of other inactive gases : helium, neon, krypton, and xenon.

The **composition of air,** freed from moisture and carbon dioxide, is roughly 4 volumes of nitrogen to 1 volume of oxygen ; the exact figures (Leduc, 1896) are :

	By weight.	By volume.
Nitrogen	75·5	78·06
Oxygen	23·2	21·00
Argon, etc.	1·3	0·94

Cavendish found that the composition of the air is sensibly constant: 20·833 vols. of oxygen and 79·167 vols. of nitrogen (including argon).

The composition of air, however, is *slightly* variable: the percentage of oxygen varies from 20·26 to 21·00, according to the locality, etc., and it is variable at different times at the same place. Air is thus entirely unsuitable as a standard of relative density.

Traces of free nitrogen are found in volcanic gases, and in the gases evolved from coal.

Combined nitrogen is widely distributed, and is a constituent of some of the most important compounds. In combination with hydrogen it forms the base **ammonia,** NH_3, occurring in the free state, and as salts in air, in water, and in volcanic districts. In combination with oxygen, nitrogen forms **nitrous,** HNO_2, and **nitric,** HNO_3, **acids,** salts of which are fairly abundant. Extensive deposits of sodium nitrate occur in Chile. Animal and vegetable organisms contain complex organic substances called **proteins,** containing an average of 16 per cent. of nitrogen. Combined nitrogen is a constituent of **explosives** such as gunpowder, nitroglycerine, gun-cotton, T.N.T., and picric acid; of **drugs** such as antipyrine, and alkaloids such as quinine and morphine; and of **colouring matters** such as indigo, and aniline dyes. Although free nitrogen is one of the most inert elements, its compounds exhibit a most wonderful diversity of properties, and enter readily into chemical reactions. The chemistry of nitrogen is therefore a subject of great interest and importance.

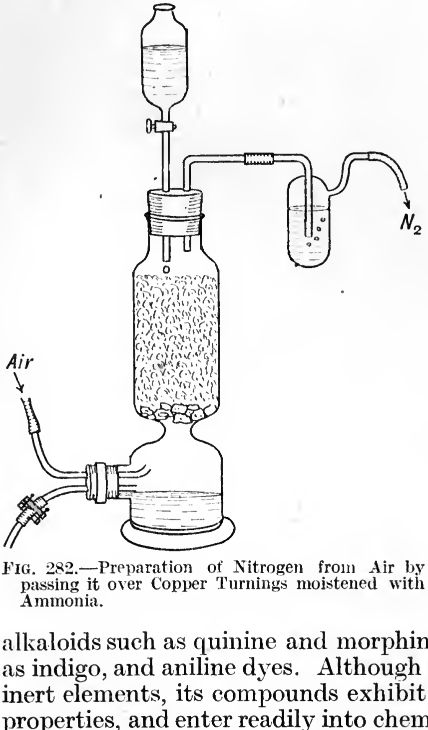


FIG. 282.—Preparation of Nitrogen from Air by passing it over Copper Turnings moistened with Ammonia.

Preparation of nitrogen from air.—Nitrogen may be prepared: (*a*) from **air,** by removal of oxygen, (*b*) from **nitrogen compounds.** That obtained from air, called **atmospheric nitrogen,** is not quite pure, since it contains about 1 per cent. of inactive gases, which give it a slightly higher density than pure or **chemical nitrogen,** prepared from compounds.

Atmospheric nitrogen is produced by the action of phosphorus, moist iron filings, liver of sulphur, etc., on air at the ordinary temperature (p. 40). Phosphorus in the form of wire removes atmospheric oxygen completely. The oxygen is also removed by an alkaline solution of pyrogallol, by an acid solution of chromous chloride (p. 166), or by a solution of cuprous chloride in hydrochloric acid or ammonia: $4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O$. Metallic copper in contact with hydrochloric acid or ammonia also removes oxygen from air.

EXPT. 194.—Pack a drying tower (Fig. 282) with clean copper turnings. Fit the upper outlet with a dropping funnel and a tube leading to a wash-bottle and pneumatic trough. Allow concentrated ammonia to drop over the copper turnings, and pass a slow stream of air upwards through the tower. The nitrogen passing on is washed with dilute sulphuric acid. A deep blue solution of cupric oxide in ammonia is formed, and may be run off from time to time by a stopcock at the base of the tower. The gas contains a trace of oxygen, which may be removed by a solution of chromous chloride. (Berthelot.)

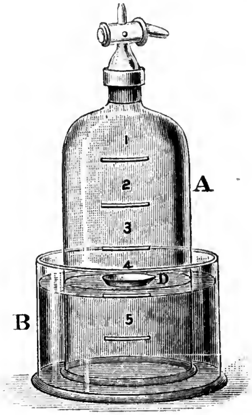


FIG. 283.—Burning Phosphorus in Air.

Oxygen is also removed from air by burning phosphorus, but not completely.

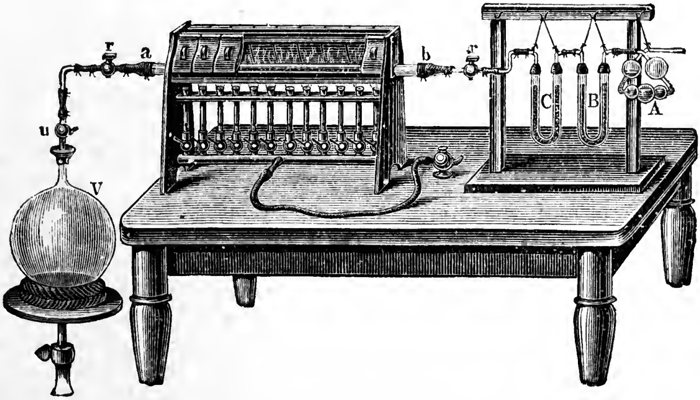


FIG. 284.—Gravimetric Composition of Air (Dumas and Boussingault).

Expt. 195.—Float a porcelain capsule containing a piece of phosphorus on water, kindle the phosphorus with a hot wire, and cover with a bell-jar divided, from the water-level, into five equal volumes by strips of label (Fig. 283). At once insert the stopper. When the phosphorus ceases to burn, the fumes of phosphorus pentoxide, P_2O_5, dissolve in the water. Allow the apparatus to cool, and equalise the water-levels. The residual gas occupies four volumes, and will be found to extinguish a lighted taper.

Oxygen is removed from air by passing the latter, dried, and freed from carbon dioxide, by solid caustic potash, over copper turnings heated to redness in a hard glass tube. From the increase in weight, due to the formation of oxide of copper, the amount of oxygen in a given volume of air, passed over from a gas-holder, may be determined. The nitrogen may be collected in an evacuated globe and weighed, and thus a gravimetric analysis of air carried out. The apparatus is shown in Fig. 284. In this way Dumas and Boussingault (1841) found that 100 parts of air contained 23·00 parts of oxygen and 77·00 parts of nitrogen by weight.

If air is bubbled through a warm concentrated solution of ammonia and the gas passed over a mixture of copper turnings and copper oxide heated to redness in a hard glass tube, the hydrogen of the ammonia is burnt by the oxygen of the air: $4NH_3 + 3O_2 = 2N_2 + 6H_2O$. The gas so prepared (Vernon Harcourt) is a mixture of atmospheric and chemical nitrogen: its density is intermediate between the densities of these two gases.

Nitrogen is manufactured either by passing air over red-hot copper, or by the fractionation of liquid air. The latter method, described on pp. 175–7, is now mostly used.

Preparation of nitrogen from its compounds.—Nitrogen may be obtained by the complete oxidation of **ammonia**: $4NH_3 + 3O_2 = 2N_2 + 6H_2O$. The oxidation may be effected by a hypochlorite or hypobromite (p. 401): $3NaOCl + 2NH_3 = 3NaCl + 3H_2O + N_2$.

Expt. 196.—To 100 c.c. of concentrated ammonia in a flask add gradually a thin paste of 40 gm. of bleaching powder, with a little milk of lime, through a thistle funnel. Nitrogen is evolved, with frothing, on warming: $3Ca(OCl)_2 + 4NH_3 = 3CaCl_2 + 6H_2O + 2N_2$.

Expt. 197.—Add 6 c.c. of bromine to a solution of 10 gm. of caustic soda in 100 c.c. of water, cooling by running water. The solution of sodium hypobromite and bromide is placed in a flask and ammonia solution dropped in; or the hypobromite is dropped on solid ammonium chloride: $3NaOBr + 2NH_3 = 3NaBr + 3H_2O + N_2$. Nitrogen is also evolved by the action of alkaline hypobromite solution on urea: $CON_2H_4 + 3NaOBr = CO_2 + N_2 + 2H_2O + 3NaBr$. The gas contains a trace of nitrous oxide, N_2O, which is removed by passing over red-hot copper.

A very convenient method for the preparation of nitrogen is the decomposition of a solution of **ammonium nitrite,** by heat: $NH_4NO_2 = N_2 + 2H_2O$. This takes place only very slowly in a faintly alkaline solution, but readily if the solution is faintly acid, so that the reaction appears to be due to the oxidation effected by free nitrous acid: $HNO_2 + NH_3 = N_2 + 2H_2O$.

EXPT. 198.—Dissolve 30 gm. of sodium nitrite in the smallest possible amount of cold water, and add a cold saturated solution of 22 gm. of ammonium chloride: $NaNO_2 + NH_4Cl \rightleftharpoons NaCl + NH_4NO_2$. Filter from the sodium chloride. Make 5 c.c. of the solution mixed with 20 c.c. of water faintly alkaline with a drop of dilute ammonia, and another 5 c.c. + 20 c.c. of water faintly acid with a drop of dilute sulphuric acid. Heat both solutions and observe the results. Heat the main quantity of the ammonium nitrite solution in a flask, and collect the gas over water. The gas contains a little nitric oxide, NO: it is purified by passing through potassium dichromate solution acidified with dilute sulphuric acid, and then over heated copper. The sodium nitrite and ammonium chloride solution may be mixed and heated directly. Pure nitrogen is also produced by passing a mixture of nitric oxide and ammonia gas through a red-hot tube:

$$6NO + 4NH_3 = 5N_2 + 6H_2O.$$

EXPT. 199.—If red crystals of **ammonium dichromate** are gently heated they undergo rapid decomposition, with evolution of nearly pure nitrogen and steam, leaving a voluminous green residue of chromium sesquioxide: $(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$.

Nitrogen is produced by the action of chlorine (or bromine) on a solution of ammonia: the reactions are usually given as:

$$2NH_3 + 3Cl_2 = 6HCl + N_2$$
$$6HCl + 6NH_3 = 6NH_4Cl.$$

The very explosive **nitrogen trichloride** is formed as an intermediate product: $2NH_3 + 6HOCl \rightleftharpoons 2NCl_3 + 6H_2O$; $NCl_3 + 4NH_3 = N_2 + 3NH_4Cl$. This substance is formed as a violently explosive oily liquid by the prolonged action of chlorine on ammonia.

EXPT. 200.—Pass a slow stream of chlorine through a wide tube into a concentrated solution of ammonia (sp. gr. 0·88) in a Woulfe's bottle (Fig. 285). As each bubble of gas passes through the liquid, there is a feeble yellow flash of light, followed by the production of dense white fumes of ammonium chloride and a brisk evolution of nitrogen. The gas so prepared contains a little oxygen: it may be passed through a second Woulfe's bottle filled with broken glass moistened with water, to filter off NH_4Cl fumes. The experiment should be interrupted after a very short time, as explosive NCl_3 is formed when ammonia is no longer in excess.

Properties of nitrogen.—Nitrogen is a colourless, odourless, tasteless gas; it does not support combustion, or respiration, although it is not poisonous; it does not turn lime-water milky. It is sparingly soluble in water, and has no action on litmus. Nitrogen can be liquefied by cooling and pressure: its critical temperature is − 146°; the critical pressure is 33 atm. The liquid is colourless, b.-pt. − 195·7°, sp. gr. at b.-pt. 0·8103. On rapid evaporation under reduced pressure it forms an ice-like solid, m.-pt. − 210·5°/86 mm. The normal density of the pure gas is 1·25107 gm./lit., whilst that of atmospheric nitrogen is 1·25718 gm./lit., *i.e.*, 0·48 per cent. heavier.

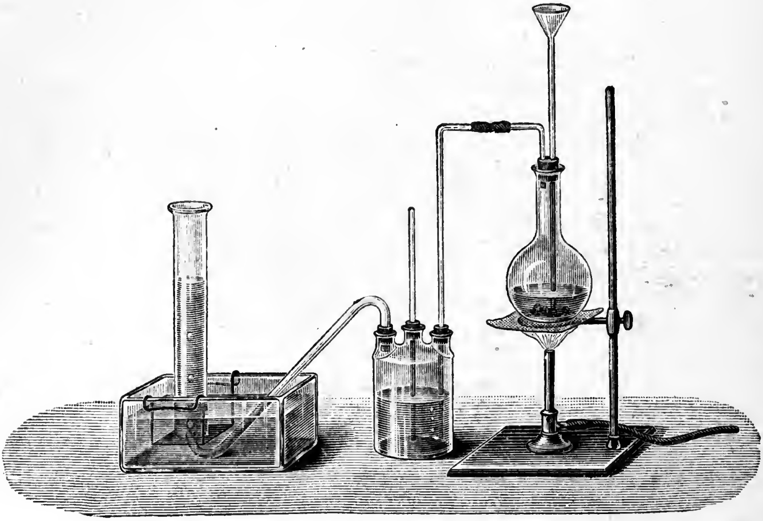
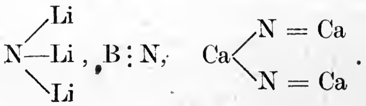


FIG. 285.—Decomposition of Ammonia by Chlorine.

Nitrogen is an inert element, but it combines directly with oxygen, hydrogen, boron, silicon, tungsten, titanium, manganese, vanadium, calcium, barium, magnesium, and lithium. In presence of alkalies, or baryta, it also combines at high temperatures with carbon to form cyanides; *e.g.*, NaCN. Compounds of elements with nitrogen are called **nitrides,** *e.g.*, Li_3N, Ca_3N_2, Mg_3N_2, BN. In these compounds nitrogen is tervalent:



Oxygen and hydrogen combine with nitrogen on sparking; the remaining nitrides are formed by passing nitrogen over the element heated to dull redness. By the action of water they give ammonia: $Ca_3N_2 + 6H_2O = 2NH_3 + 3Ca(OH)_2$. When nitrogen is passed over strongly-heated calcium carbide it is rapidly absorbed, with formation of a mixture of **calcium cyanamide** and graphite: $CaC_2 + N_2 = CaCN_2 + C$.

EXPT. 201.—Burn a piece of magnesium ribbon in air. Heat the white product, containing MgO and Mg_3N_2, with water in a test-tube, and hold a piece of moist red litmus paper in the tube. It is turned blue by the ammonia evolved.

EXPT. 202.—Heat some magnesium powder in nitrogen in the short limb of a bent hard glass tube over mercury. The mercury slowly rises, owing to absorption of nitrogen.

Active nitrogen.—Just as ozone is produced from oxygen by the action of an electric discharge, an active form of nitrogen is obtained by subjecting a current of nitrogen, drawn through a tube at low pressure, to a high tension discharge. The gas travelling beyond the portion of the tube in which the discharge occurs glows with a greenish-yellow light. White phosphorus is converted into red phosphorus, and sodium and mercury form compounds at 150° when exposed to the gas. Nitric oxide forms nitrogen dioxide. Strutt (1911), to whom these discoveries are due, regards the active nitrogen as monatomic, since the gas is not condensed in liquid air. Recent experiments indicate that a trace of oxygen is necessary in the production of active nitrogen, although an excess destroys it. It is without action on hydrogen.

Compounds of nitrogen and hydrogen.—Nitrogen forms three well-defined compounds with hydrogen:

Ammonia,	NH_3;
Hydrazine,	N_2H_4;
Hydrazoic acid,	N_3H.

The compounds N_2H_2 (**di-imide**), and N_4H_4 (**buzylene**), are known only in organic derivatives. Compounds N_4H_5 and N_5H_5 exist as salts of hydrazoic acid (p. 559).

Ammonia and **hydrazine** are **basic substances,** combining with acids to form **ammonium** and **hydrazine salts**; *e.g.*, $NH_3{\cdot}HCl$ or NH_4Cl; $N_2H_4{\cdot}HCl$ or N_2H_5Cl, and $N_2H_4{\cdot}2HCl$ or $N_2H_6Cl_2$. **Hydrazoic acid** is an **acid**, dissolving metals with evolution of hydrogen, and forming salts which are ionised in solution, *e.g.*, $NaN_3 \rightleftharpoons Na^{\cdot} + N_3'$. The ion N_3' is univalent.

If the hydrogen atoms of ammonia are replaced by hydroxyl groups, the following compounds are obtained:

NH_2OH, **hydroxylamine,** a base, forming salts, *e.g.*, $NH_2{\cdot}OH,HCl$;
$NH(OH)_2$, **dihydroxylamine,** unknown in the free state;
$N(OH)_3$, **orthonitrous acid,** the hypothetical ortho-acid corresponding with ordinary nitrous acid, HNO_2.

Ammonia, NH_3.—Traces of ammonia occur in the atmosphere: bottles containing hydrochloric acid become coated after a time with ammonium chloride. **Ammonium chloride,** NH_4Cl, and **sulphate,** $(NH_4)_2SO_4$, occur in volcanic districts; ammonia also accompanies boric acid in the *fumaroles* of Tuscany, and may have been formed by the decomposition of boron nitride: $BN + 3H_2O = H_3BO_3 + NH_3$. Small quantities of ammonium salts occur in plants and animals (*e.g.*, in blood, and in urine as *microcosmic salt,* $NaHNH_4PO_4$), in the soil, and in natural waters (as nitrite and nitrate).

Ammonia is obtained as a by-product in the destructive distillation of organic matter containing nitrogen (coal, horn, bones, etc.). On the small scale, the yield of ammonia is greater if the materials are mixed with *soda-lime,* prepared by slaking quicklime with caustic soda solution, and heating till dry.

EXPT. 203.—Heat a few pieces of feather, or a little glue, with soda-lime in a test-tube, and test the vapours: (*a*) with moist red litmus paper, which is turned blue; (*b*) with a glass rod dipped in concentrated hydrochloric acid, which evolves white fumes of ammonium chloride NH_4Cl; (*c*) with paper dipped in mercurous nitrate solution, which is turned black. Repeat the experiment with filter-paper (free from nitrogen) without soda-lime, but test with blue litmus paper. In this case acetic acid, $C_2H_4O_2$, is formed.

Ammonium chloride, NH_4Cl, is described by the Latin Geber, and was called *sal armoniacum.* It appears to have been derived from the volcanoes of Central Asia. Later, it was brought from Egypt, and seems to have been prepared from the soot formed on burning camels' dung. Its name was changed to *sal ammoniacum,* previously given to common salt found in the Libyan Desert near the ruins of the temple of Jupiter Ammon (Greek *ammos* = sand). This name was subsequently abbreviated to *sal ammoniac.*

A solution of ammonium carbonate, $(NH_4)_2CO_3$, was also obtained by distilling putrefied urine: CON_2H_4 (urea) $+ 2H_2O = (NH_4)_2CO_3$; or by the dry distillation of bones, hoofs, horns, etc.; it was known as *spirit of hartshorn, sal volatile,* or the *volatile alkali.* By distilling this with quicklime, a solution of *caustic volatile alkali,* NH_4OH, was obtained, described in Kunckel's posthumous works (1716). Gaseous ammonia was first obtained by Priestley in 1774, by collecting over mercury; he called it *alkaline air*, and found that when electric sparks were passed through it double the volume of a combustible gas was formed: $2NH_3 = N_2 + 3H_2$. Berthollet (1785) showed that nitrogen and hydrogen were formed in this decomposition; the result was confirmed, and the formula NH_3 established, by Austin (1788), Davy (1800), and Henry (1809).

Ammonia is formed from its elements when these are sparked together: $N_2 + 3H_2 \rightleftharpoons 2NH_3$. This appears to have been discovered by Regnault (1840); it was confirmed by Deville (1874), who pointed out that sparks will bring about both the formation and the decomposition of ammonia. The reaction is reversible, and a state of equilibrium is set up in which 6 per cent. of NH_3 exists with 94 per cent. of the uncombined gases. If the mixture $N_2 + 3H_2$, and pure ammonia, respectively, are exposed to prolonged sparking, contraction ensues in the first case and expansion in the second, until the volumes and compositions are the same:

$$\underset{\text{6 per cent.}}{2NH_3} \rightleftharpoons \underset{\text{94 per cent.}}{N_2 + 3H_2}.$$

Expt. 204.—Spark a mixture of nitrogen and hydrogen over mercury in a eudiometer containing a little concentrated sulphuric acid. Observe the gradual contraction, owing to formation of ammonia, which is withdrawn by the sulphuric acid.

Synthetic ammonia.—The direct combination of nitrogen and hydrogen is utilised in the **Haber process** (1905) for the synthetic production of ammonia. Since a diminution of volume occurs in the reaction: $2N_2 + 3H_2 = 2NH_3$, the amount of ammonia formed in equilibrium will increase with the pressure.

Since heat is evolved in the reaction, the amount of ammonia in the equilibrium state will diminish with rise of temperature. At very high temperatures (above 1000°) heat seems to be absorbed in the reaction, and the amount of ammonia then increases with the temperature. This explains its formation in the electric spark.

In order to obtain appreciable amounts of ammonia, the mixture of nitrogen and hydrogen, which must be very pure, is circulated by pumps, under 100–200 atm. pressure, or even 1000 atm. in Claude's process, over a catalyst, which may be a mixture of finely-divided iron and molybdenum, and the ammonia formed in each circulation is removed by cooling and liquefaction, or by absorption in water. The argon present in the atmospheric nitrogen, which accumulates, is blown off from time to time. The percentages of ammonia, by volume, present in equilibrium under various conditions are given in the table below :

Pressure in atm.	Temperature °. 550	650	750	850	950
1	0·077	0·032	0·016	0·009	0·005
100	6·7	3·02	1·54	0·874	0·542
200	11·9	5·71	2·99	1·68	1·07

In 1910 the Haber process was adopted by the Badische Co. in Germany; in 1916 the production of ammonium sulphate, of the highest degree of purity, was 500,000 tons annually, at a cost of £6 per ton, as compared with about £10 per ton by other methods.

The cyanamide process.—Another process which is largely used for the **fixation of atmospheric nitrogen** is the **cyanamide process** of Frank and Caro (1895).

Nitrogen is passed over crushed calcium carbide with some calcium chloride or fluoride, heated to 1100°, either by carbon rods heated electrically inside drums of carbide, or by dropping the carbide continuously through electric arcs. **Calcium cyanamide** mixed with graphite is formed as a dark grey mass: $CaC_2 + N_2 = CaCN_2 + C$. This substance is a derivative of **cyanamide,** the amide of hydrocyanic acid, *i.e.*, hydrocyanic acid in which an atom of hydrogen is replaced by the **amino-group** :

$$\underset{\text{Hydrocyanic acid}}{HCN} \rightarrow \underset{\text{Cyanamide}}{NH_2{\cdot}CN} \rightarrow \underset{\text{Calcium cyanamide}}{NCa{\cdot}CN} \text{ or } Ca{:}N{\cdot}N{\vdots}C.$$

The "cyanamide" is agitated with cold water to remove unchanged carbide, and then stirred with water and a little sodium carbonate in large iron autoclaves, *i.e.*, pressure digesters, into which steam is blown until the pressure rises to 3–4 atm. The pressure then rises automatically to 12–14 atm., owing to production of ammonia, which is blown off, with some steam, through condensers, the solution formed being treated in a still with steam to drive out the gas: $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$. The sludge of calcium carbonate, lime, and graphite (from the cyanamide) is thrown away.

The **Bucher process** (1917) consists in passing nitrogen over an intimate mixture of sodium carbonate, charcoal or coke, and iron filings. Sodium cyanide is formed, the iron acting as a catalyst :

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO.$$

Steam is then blown over the mass, when sodium formate and ammonia are produced: $NaCN + 2H_2O = H{\cdot}COONa + NH_3$. This process, owing to technical difficulties, has not been a success.

In the **Serpek process,** formerly worked in France, **aluminium nitride,** AlN, was formed by passing nitrogen over a mixture of coke and bauxite (native aluminium oxide) in a revolving electric furnace at 1800°: $Al_2O_3 + 3C + N_2 = 2AlN + 3CO$. The product was decomposed by boiling water at 4–6 atm., with formation of ammonia: $2AlN + 6H_2O = 2Al(OH)_3 + 2NH_3$.

Preparation of ammonia in the laboratory.—In the laboratory, ammonia gas is prepared by heating ammonium chloride or sulphate with dry slaked lime:

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

EXPT. 205.—Mix 50 gm. of powdered ammonium chloride with 150 gm. of powdered slaked lime in a mortar, transfer to a 250 c.c. flask, and fill up the latter with small lumps of quicklime. Fit a cork and delivery tube, leading to a drying tower filled with lumps of quicklime or caustic soda, heat the flask on wire gauze, and collect the gas by upward displacement (Fig. 286), or over mercury. The jar is full when a piece of moist red litmus paper held near the mouth is turned strongly blue. After drying with caustic soda or potash, the gas may be dried with phosphorus pentoxide. Concentrated sulphuric acid reacts violently with the gas, forming ammonium sulphate, $(NH_4)_2SO_4$, and calcium chloride absorbs it, forming a compound, $CaCl_2,8NH_3$; hence these reagents cannot be used to dry ammonia.

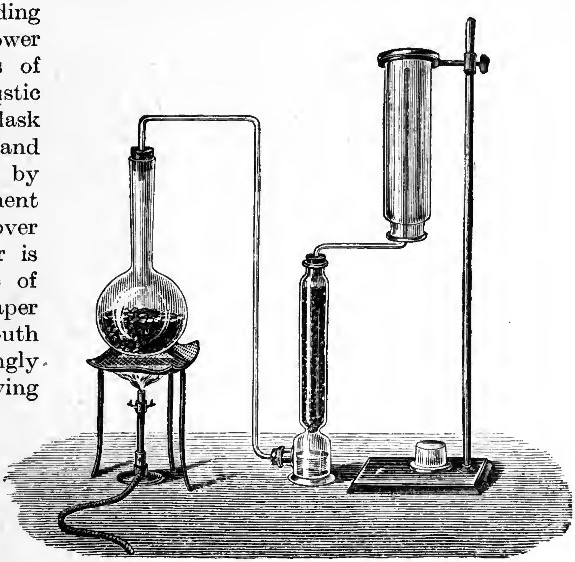


FIG. 286.—Preparation of Ammonia Gas.

Ammonia is also produced by heating ammonium sulphate: $(NH_4)_2SO_4 = NH_3 + NH_4HSO_4$; microcosmic salt: $NH_4HNaPO_4 = NH_3 + H_2O + NaPO_3$ (sodium metaphosphate); or ammonium phosphate: $(NH_4)_3PO_4 = 3NH_3 + H_2O + HPO_3$. It is also formed when ammonium salts are heated with a concentrated solution of caustic soda: $(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O + 2NH_3$, or when ammonium chloride is heated with litharge: $PbO + NH_4Cl \rightleftharpoons Pb(OH)Cl + NH_3$. A regular stream of gas is evolved on warming 170 gm. of ammonium sulphate with 250 c.c. of 50 per cent. caustic soda solution.

Expt. 206.—The most convenient method is to warm the concentrated aqueous solution (*liquor ammoniæ fortis*, sp. gr. 0·88), alone or after saturation with fused calcium chloride, in a flask; the gas is dried with quicklime. The solution may also be dropped on lumps of caustic soda.

Ammonia is formed by the reduction of oxygen compounds of nitrogen with nascent hydrogen. Thus, if a mixture of hydrogen and nitric oxide (or a higher oxide of nitrogen, or even nitric acid vapour) is passed over heated spongy platinum, ammonia is produced: $2NO + 5H_2 = 2NH_3 + 2H_2O$. Dilute nitric acid in presence of dilute sulphuric acid is reduced by zinc to ammonium sulphate: $HNO_3 + 8H = NH_3 + 3H_2O$. Sodium nitrate, or more readily sodium nitrite, is reduced by zinc and hot caustic soda solution, giving pure ammonia. Aluminium may be used instead of zinc, but nitrates are most easily reduced in alkaline solution by powdered Devarda's alloy, containing 45 parts of Al, 50 parts of Cu, and 5 parts of zinc.

Expt. 207.—Dissolve 10 gm. of sodium nitrite and 10 gm. of caustic soda in 50 c.c. of water and heat with a few pieces of granulated zinc in a flask. Ammonia is given off, turning red litmus paper blue. This method is used for the estimation of nitrates or nitrites, the ammonia being distilled into standard acid.

Properties of ammonia.—Ammonia is a colourless gas, lighter than air (sp. gr. 0·59, air = 1), normal density 0·7708 gm./lit. It is easily liquefied by cold or pressure, forming a colourless liquid, b.-pt. − 33·5°, freezing to an ice-like solid, m.-pt. − 77°. The critical temperature is 130°, and the critical pressure 115 atm. The liquid may be obtained by cooling with a mixture of ice and crystalline calcium chloride; it is produced on a large scale by compressing the gas into steel coils cooled with water, and is sent out in steel cylinders holding 25, 50, or 100 lb. (*anhydrous ammonia*). The gas has a characteristic pungent smell, and is readily soluble in water. The solution is alkaline.

Expt. 208.—Fit a round-bottom flask full of ammonia gas with a cork and tube dipping into water coloured with red litmus. Proceed as in Expt. 103: the water rushes in as a fountain, and the litmus is turned blue (Fig. 127).

The aqueous solution is prepared by passing the gas into cold distilled water; the flask must be kept cool by running water over the outside from a perforated ring of lead pipe (Fig. 126), since a considerable amount of heat is evolved. The liquid also expands considerably. The saturated solution has a sp. gr. of 0·884 and contains 36 per cent. of NH_3 :

Sp. gr.	Per cent. of NH_3	Sp. gr.	Per cent. of NH_3
0·8844	36·0	0·9251	20·0
0·8864	35·0	0·9414	15·0
0·8976	30·0	0·9593	10·0
0·9106	25·0	0·9790	5·0

The aqueous solution is alkaline : it contains **ammonium hydroxide,** together with much free ammonia : $NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'$. By strong cooling, the crystalline hydrates NH_3,H_2O, or NH_4OH, **ammonium hydroxide,** m.-pt. $-79·3°$, and $2NH_3,H_2O$ or $(NH_4)_2O$, **ammonium oxide,** m.-pt. $-78·6°$, are obtained. A crystalline **ammonium peroxide,** $(NH_4)_2O_2$, is formed by the action of ammonia on cold concentrated hydrogen peroxide.

Ammonia is soluble in alcohol : 1 litre of alcohol dissolves 130 gm. of NH_3 at 0°. The solubility of ammonia in water obeys Henry's law only above 100° : all the gas is expelled on boiling a solution. Since a considerable amount of heat is evolved on solution of the gas, there is a large fall of temperature when the gas is removed from the solution by a stream of air.

Expt. 209.—Pass a rapid stream of air from bellows through a little concentrated ammonia in a small flask standing on a wetted block of wood. The flask is frozen firmly to the block. A temperature of $-40°$ (at which mercury freezes) can be reached by rapid evaporation. The method has been applied in some ice machines (Carré's).

The evaporation of liquid ammonia (not the solution) in steel pipes is used in **freezing machines** (p. 202). The gas produced is again liquefied by compression into steel coils immersed in cold water.

If ammonia is passed over heated potassium or sodium, one-third of the hydrogen is replaced by the metal, and **potassamide,** KNH_2, or **sodamide,** $NaNH_2$, is formed. These are white solids when pure. They contain the univalent **amino-group,** NH_2-.

Expt. 210.—Pass ammonia, dried over quicklime or caustic potash, over a piece of potassium heated in a hard glass bulb tube. The metal boils, emitting a green vapour, and reaction then begins. The hydrogen evolved may be kindled at the end of the tube, and a brown mass of impure potassamide is left in the tube.

The compounds are violently decomposed by water, with evolution of ammonia : $NaNH_2 + HOH = NaOH + NH_3$.

Ammonia is not-combustible, and does not support combustion, but the flame of a taper, before it is extinguished in the gas, is surrounded by a large greenish-yellow flame, due to decomposition of ammonia by heat: $2NH_3 = N_2 + 3H_2$. Ammonia burns in oxygen with a greenish-yellow flame: $4NH_3 + 3O_2 = 6H_2O + 2N_2$. The gas is first decomposed to a large extent into its elements.

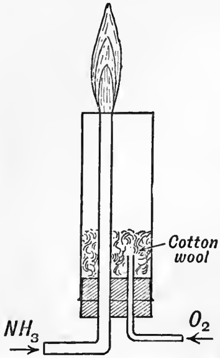


FIG. 287.—Combustion of Ammonia in Oxygen.

EXPT. 211.—Pass a current of ammonia through a tube surrounded by a wider tube through which oxygen gas is passing (Fig. 287). If a taper is held over the tubes, the ammonia burns with a large, double-cone, yellowish flame.

EXPT. 212.—Prepare mixtures of oxygen and ammonia gas over mercury in four strong glass tubes, 8 in. long and 1 in. diameter, sealed at one end, in the proportions: $4NH_3 + 3O_2$; $4NH_3 + 5O_2$; $NH_3 + 5O_2$; $2NH_3 + 13O_2$. Ignite the mixtures with a taper. The first two burn with violent explosions; the remaining mixtures explode less violently, and with excess of oxygen a little red fume of NO_2 and white fumes of ammonium nitrite and nitrate are formed.

EXPT. 213.—Pass oxygen through a little concentrated ammonia warmed in a 100 c.c. conical flask, and suspend a red-hot spiral of platinum wire in the flask. The mixture of ammonia and oxygen explodes feebly: $4NH_3 + 3O_2 = 6H_2O + 2N_2$. The wire cools, owing to combustion ceasing, but after a short time there is another explosion, when the gas mixture is renewed. During oxidation without explosion, red fumes of oxides of nitrogen and white fumes of ammonium nitrate are formed:

$$4NH_3 + 5O_2 = 4NO + 6H_2O;\ 2NO + O_2 = 2NO_2;$$
$$4NO_2 + O_2 + 2H_2O + 4NH_3 = 4NH_4{\cdot}NO_3.$$

Ammonia is readily absorbed by dry silver chloride, forming the compounds $AgCl,3NH_3$ below 15°, and $2AgCl,3NH_3$ above 20°. If the compound is sealed up in one limb of a bent tube (Fig. 124) and gently heated, liquid ammonia collects in the other limb, immersed in a freezing mixture. On allowing the silver chloride to cool the ammonia is reabsorbed.

Ammonia is not easily decomposed by heat, especially if diluted with an indifferent gas. A mixture of ammonia and air may also be passed through an iron tube heated to dull redness without appreciable decomposition.

The composition of ammonia.—If electric sparks are passed for some time through ammonia gas in a eudiometer, it will be found that the volume is nearly doubled. If oxygen is now added and a spark passed, water is formed, and two-thirds of the contraction is equal to the volume of the hydrogen. *E.g.*,

Volume of ammonia taken = 20 c.c.
Volume of gas after sparking = 40 c.c.
Volume after addition of oxygen = 120 c.c.
Volume after explosion = 75 c.c.

$\therefore$ contraction on explosion with oxygen $= 120 - 75 = 45$ c.c. $\therefore$ volume of hydrogen $= \frac{2}{3} \times 45 = 30$ c.c. $\therefore$ volume of nitrogen $= 40 - 30 = 10$ c.c. Thus 1 vol. of nitrogen + 3 vols. of hydrogen = 2 vols. of ammonia (Henry, 1809).

If a concentrated solution of ammonia containing a little ammonium sulphate (*not* chloride, as explosive nitrogen chloride may be formed) is electrolysed, 1 vol. of nitrogen collects at the anode to 3 vols. of hydrogen at the cathode.

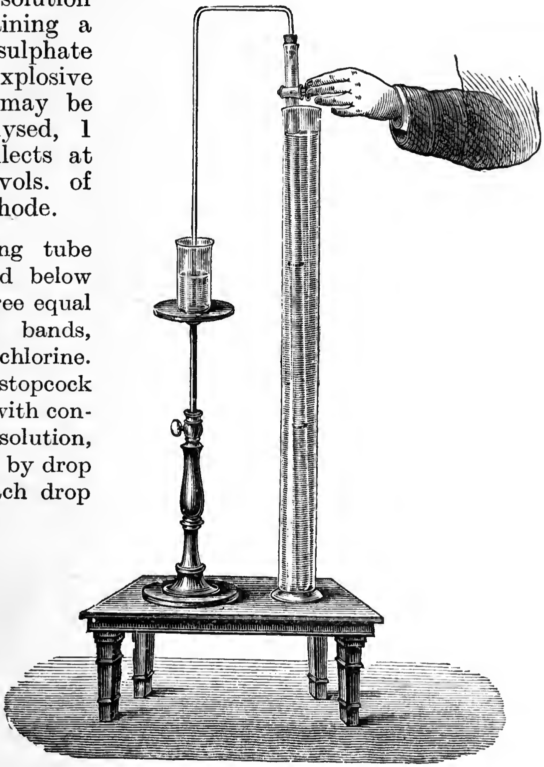


Fig. 288.—Volumetric Composition of Ammonia (Hofmann).

Expt. 214.—A long tube (Fig. 288) is divided below the stopcock into three equal volumes by rubber bands, and is filled with chlorine. The tube above the stopcock is two-thirds filled with concentrated ammonia solution, which is added drop by drop to the chlorine. Each drop reacts with a yellowish-green flame, and the formation of white clouds of ammonium chloride ($2NH_3 + 3Cl_2 = 6HCl + N_2$; $HCl + NH_3 = NH_4Cl$; *cf.* p. 555). The fumes are washed down by shaking, and the tube is warmed in hot water to expel the nitrogen from the liquid. Dilute sulphuric acid is then added to fix the excess of ammonia. The tube is cooled by immersing in a large cylinder of water, and the upper part above the tap is fitted with a cork and siphon tube dipping into previously boiled water, the whole being filled with water, as shown. On opening the tap, water rushes into the tube, and when the levels are equalised it is found that the residual nitrogen occupies 1 vol.

The 3 vols. of chlorine have combined with 3 vols. of hydrogen from the ammonia to form HCl, ∴ 1 vol. of nitrogen is combined in ammonia with 3 vols of hydrogen. (Hofmann.)

The **gravimetric analysis** of ammonia is performed by passing a measured volume of dry ammonia, the weight of which under the given conditions may be calculated from the density, over red-hot copper oxide in a hard glass tube. The water formed is collected in weighed calcium chloride tubes. The nitrogen passing on is collected and measured, and its weight calculated from the density. In this way the ratio N : H is found to be 14 : 3. This, taken in conjunction with the density of ammonia, and the volume ratio, gives the formula NH_3. The relative density of the gas is 8·552, corresponding with the molecular weight 17·10, *i.e.*, approximately (since the gas does not obey Boyle's law exactly) with $NH_3 = 13{\cdot}897 + 3 = 16{\cdot}906$. The **atomic weight of nitrogen** has been determined from the analysis of ammonia: $N = 13{\cdot}897$, directly with respect to hydrogen. The previous determinations, referred to $O = 16$, involved the atomic weight of silver through the ratio: $Ag : AgNO_3$.

By-product ammonia.—Large quantities of ammonia and ammonium salts, especially ammonium sulphate, are recovered as by-products in the manufacture of gas or coke from coal. Bituminous coal contains about 1 per cent. of nitrogen, a portion of which is recovered in destructive distillation (p. 680). The nitrogen then comes over mainly in the form of ammonia, although a little hydrocyanic acid, HCN, is present. The ammonia combines with sulphuretted hydrogen, carbon dioxide, and sulphur dioxide, which are also produced, to form salts, which dissolve in the water in the coolers and scrubbers, giving **ammoniacal liquor.** The average yield of ammonia in gas-works and coke-ovens is 20–25 lb. of ammonium sulphate per ton of coal, representing less than 20 per cent. of the nitrogen in the latter. Most of the nitrogen remains in the coke, and a further supply of ammonia, reaching a total recovery of 60 per cent. of the nitrogen in the fuel, may be obtained by carbonising the latter in a current of steam, or by blowing steam through the coke (p. 706).

Ammoniacal liquor contains tar and organic compounds, and ammonium salts of two kinds: (1) **Volatile salts,** expelled by hydrolysis on boiling alone; *e.g.*, ammonium carbonates, sulphide and hydrosulphide, cyanide, acetate (?), and hydroxide. (2) **Fixed salts,** not decomposed by boiling, but decomposed by lime; *e.g.*, ammonium sulphate, sulphite, thiosulphate, thiocarbonate, chloride, thiocyanate, and ferrocyanide. The total ammonia may be about 17 gm. per litre.

The ammonia is recovered from this liquor by means of **ammonia stills,** in which the liquor is heated by steam to drive out the free ammonia, or that produced by the hydrolysis of the volatile salts, and the residue is then treated with milk of lime and additional steam to decompose the fixed salts. *E.g.*, $NH_4HS \rightleftharpoons NH_3 + H_2S$; $2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$.

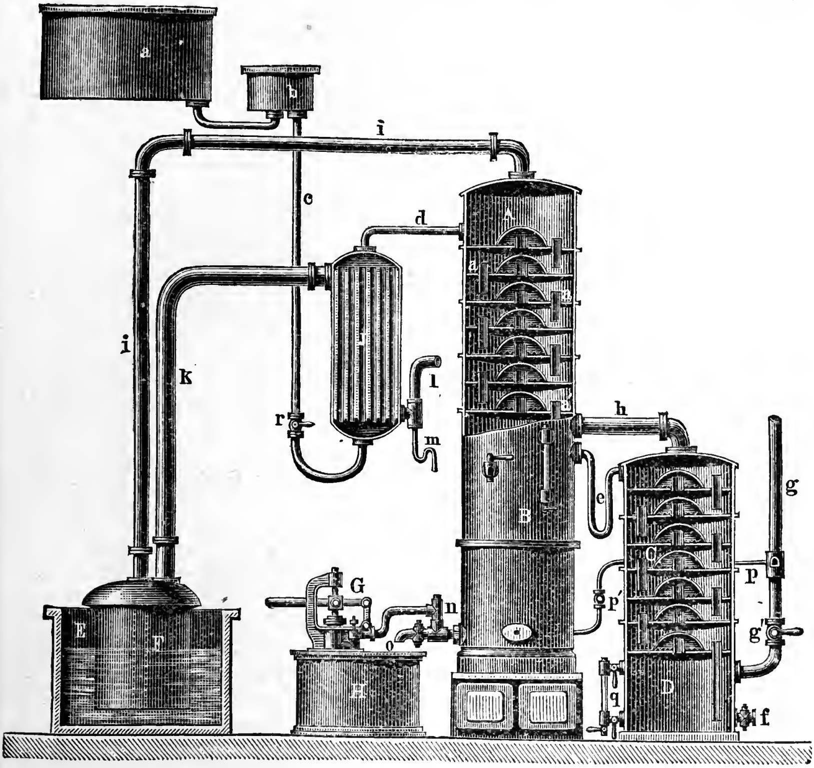


FIG. 289.—Feldman's Ammonia Still.

A typical still, the **Feldman still,** is shown in Fig. 289. It consists of two iron columns containing perforated plates. In the first column, *A*, the ammoniacal liquor is treated with steam to drive out the volatile ammonia. Milk of lime from H is then added in the lower part, *B*, of this column, and the sludge allowed to settle. The clarified liquor then passes to the second column, *C*, where the ammonia set free by the lime is driven out by steam.

The ammonia from the still may be bubbled through 60 per cent. sulphuric acid in a lead-lined tank, *E*, when crystals of **ammonium sulphate** separate; these after draining contain 93–99 per cent. of $(NH_4)_2SO_4$ with a little tarry matter and free acid. If the gas is passed through a washer containing milk of lime, to remove sulphuretted hydrogen, and then through charcoal, or a heavy oil washer, to remove tarry matter, it may be dissolved in water to form a solution. Usually "25 per cent. liquor" is made; the special strong liquor of density 0·884 (35 per cent. NH_3) requires very careful cooling in its preparation. About 400,000 tons of by-product ammonium sulphate are annually prepared in Great Britain: it is nearly all used in agriculture as a fertiliser.

Attempts have recently been made to recover ammonia from the crude gas, from gas-works or coke-ovens, by passing the gas through sulphuric acid without previous deposition of ammoniacal liquor. This **direct process** is working in connection with coke-ovens at Skinningrove and elsewhere.

Hydroxylamine, $NH_2\cdot OH$.—Hydroxylamine, or **hydroxy-ammonia,** $NH_2\cdot OH$, was discovered by Lossen in 1865. He obtained its **salts** by two methods:

1. By the reduction of nitric oxide, NO, with nascent hydrogen: $NO + 3H = NH_2\cdot OH$.

A stream of nitric oxide, from the action of dilute nitric acid on copper, is passed through a series of flasks containing granulated tin, concentrated hydrochloric acid, and a few drops of platinic chloride. Reduction occurs, with the formation of ammonium chloride, NH_4Cl, and **hydroxylamine hydrochloride,** $NH_2\cdot OH,HCl$ [or **hydroxylammonium chloride,** $NH_3(OH)Cl$]. The solution is treated with sulphuretted hydrogen to precipitate tin as stannous and stannic sulphides, filtered, and evaporated to dryness. The residue is extracted first with cold, then with boiling absolute alcohol, which dissolves the hydroxylamine salt, but not the ammonium chloride. Hydroxylamine hydrochloride is then precipitated from the alcoholic solution by adding ether.

2. By the reduction of ethyl nitrate, $C_2H_5NO_3$, by nascent hydrogen: $C_2H_5NO_3 + 6H = C_2H_5\cdot OH + NH_2\cdot OH + H_2O$.

Thirty gm. of $C_2H_5NO_3$, 120 gm. of granulated tin, and 40 gm. of HCl (sp. gr. 1·06) are mixed, when reaction occurs spontaneously. The solution is treated as in (1). This is a convenient method of preparation.

3. Hydroxylamine salts may be prepared by the electrolytic reduction of nitric acid (Tafel, 1902):

$$HNO_3 + 6H = NH_2{\cdot}OH + 2H_2O.$$

A cooled lead anode is separated by a porous pot from an amalgamated lead beaker serving as a cathode, the whole being cooled by ice. Fifty per cent. sulphuric acid is placed in each compartment, and 50 per cent. nitric acid added drop by drop to the cathode compartment. **Hydroxylamine sulphate,** $NH_2{\cdot}OH,H_2SO_4$, is formed.

4. A very convenient method of preparing hydroxylamine salts is by the interaction of nitrites and sulphites in solution (Raschig, 1888):

$$NaNO_2 + NaOH + 2SO_2 + 2H_2O = NH_2{\cdot}OH,H_2SO_4 + Na_2SO_4.$$

EXPT. 215.—A concentrated solution of 2 mols. of commercial $NaNO_2$ + 1 mol. of Na_2CO_3 is treated with sulphur dioxide at − 2° till just acid, keeping well stirred. The solution now contains **sodium hydroxylamine disulphonate,** $HO{\cdot}N(SO_3Na)_2$, *i.e.*, $HO{\cdot}NH_2$ with 2H replaced by $2SO_3Na$. If the solution is warmed with a few drops of sulphuric acid, hydrolysis occurs, and **sodium hydroxylamine monosulphonate,** $HO{\cdot}NH(SO_3Na)$, is formed. If kept at 90–95° for two days, further hydrolysis occurs, with formation of **hydroxylamine sulphate,** $NH_2{\cdot}OH,H_2SO_4$. The solution is neutralised with soda, evaporated to a small bulk, and cooled to 0°, when Glauber's salt, $Na_2SO_4,10H_2O$, crystallises out. The filtrate on further evaporation deposits hydroxylamine sulphate, which is rapidly recrystallised from water.

The reaction occurs in three stages, as follows:

(*a*) $NaNO_2 + 3NaHSO_3 = HO{\cdot}N(SO_3Na)_2 + Na_2SO_3 + H_2O$
Sodium hydroxylamine disulphonate.

(*b*) $HO{\cdot}N(SO_3Na)_2 + H_2O = HO{\cdot}NH(SO_3Na) + NaHSO_4$
Sodium hydroxylamine monosulphonate.

(*c*) $HO{\cdot}NH(SO_3Na) + H_2O = HO{\cdot}NH_2 + NaHSO_4$
Hydroxylamine.

By these methods **salts of hydroxylamine** are produced: if caustic potash is added to a solution of a salt, free hydroxylamine is first formed, but is unstable: $3NH_2{\cdot}OH = NH_3 + 3H_2O + N_2$.

Anhydrous hydroxylamine, $NH_2{\cdot}OH$, was prepared by Lobry de Bruyn in 1891 by treating a solution of the hydrochloride in methyl alcohol with a solution of sodium methoxide in methyl alcohol (obtained by dissolving sodium in the alcohol: $2CH_3{\cdot}OH + 2Na = 2CH_3ONa + H_2$), filtering off the sodium chloride, and distilling under reduced pressure (40 mm.): $CH_3ONa + NH_2{\cdot}OH,HCl = CH_3{\cdot}OH + NaCl + NH_2{\cdot}OH$. Crismer (1891) distilled the double compound $ZnCl_2,2NH_2\cdot OH$ (obtained by boiling zinc oxide with a solution of hydroxylamine hydrochloride) at 120°, either alone or with aniline. Anhydrous hydroxylamine is also formed by heating the orthophosphate to 135° under very low pressure (13 mm.): $(NH_4O)_3PO_4 = H_3PO_4 + 3NH_3O$.

Properties of hydroxylamine.—Pure hydroxylamine forms colourless, odourless crystals, sp. gr. 1·3, m.-pt. 33°. It is very deliquescent. It may be distilled under reduced pressure (55–58°/22 mm.), but explodes when heated at the ordinary pressure. The vapour density corresponds with NH_3O. Above 15° it slowly decomposes, evolving nitrogen and nitrous oxide. Aqueous solutions containing up to 60 per cent. are fairly stable. The vapour explodes in contact with air at 60–70°. The solution is strongly basic and precipitates many metals (Zn, Al) as hydroxides.

Hydroxylamine and its salts in aqueous solution act as powerful **reducing agents.** They precipitate red cuprous oxide from copper sulphate in alkaline solution, purple metallic gold from gold chloride, and in *acid* solutions reduce ferric to ferrous salts:

$$\begin{aligned} 2NH_3O + 4CuO &= N_2O + 3H_2O + 2Cu_2O \\ 4FeCl_3 + 2NH_3O &= N_2O + 4FeCl_2 + 4HCl + H_2O. \end{aligned}$$

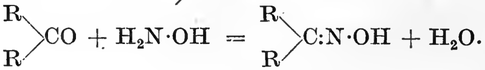
In *alkaline* solution, hydroxylamine oxidises ferrous hydroxide to ferric hydroxide, with formation of ammonia:

$$2Fe(OH)_2 + NH_3O + H_2O = 2Fe(OH)_3 + NH_3.$$

The salts on heating with nitric acid evolve nitric oxide: $NH_3O + HNO_3 = 2NO + 2H_2O$. When treated with a nitrite and acidified, they evolve nitrous oxide on warming. **Hyponitrous acid,** $H_2N_2O_2$, is formed as an intermediate product:

$$HO\cdot NH_2 + \underset{\text{Nitrous acid}}{ON\cdot OH} = \underset{\text{Hyponitrous acid}}{HO\cdot N{:}N\cdot OH} + H_2O = N_2O + 2H_2O.$$

Hydroxylamine reacts with organic substances containing the aldehyde, $-COH$, or ketone $>CO$, groups, forming **oximes**:



$$\begin{matrix}R\\R\end{matrix}\!\!>CO + H_2N\cdot OH = \begin{matrix}R\\R\end{matrix}\!\!>C{:}N\cdot OH + H_2O.$$

On hydrolysis, these give hydroxylamine. Fulminic acid, $C{:}N\cdot OH$, on boiling with hydrochloric acid gives hydroxylamine. If a neutral solution containing a hydroxylamine salt is treated with sodium nitroprusside, and a little caustic soda, a beautiful red colour appears on boiling (test).

Nitrogen trichloride.—Dulong (1811) by the action of chlorine on a solution of ammonium chloride obtained a yellow oily liquid which was violently explosive. He lost an eye and a finger in the research. Davy and Faraday (1813) obtained the compound by the action of excess of chlorine on ammonia, and concluded that its formula was NCl_4. Balard prepared it by the action of hypochlorous acid on ammonia, and Böttger and Kolbe found that it separated at the anode in the electrolysis of ammonium chloride solution at 28°. The substance is **nitrogen trichloride**, NCl_3:

$$3Cl_2 + 3H_2O \rightleftharpoons 3HOCl + 3HCl$$
$$NH_4Cl + 3HOCl \rightleftharpoons NCl_3 + 3H_2O + HCl.$$

Nitrogen trichloride may be prepared by inverting a flask of chlorine over a 25 per cent. freshly prepared solution of ammonium chloride, a lead saucer being placed under the mouth of the flask (Fig. 290). The chlorine is absorbed, and oily drops of the trichloride float on the surface of the solution. These fall into the lead saucer, which should be removed when a little liquid has collected in it. If a little turpentine is passed into the flask, a violent explosion results, the glass being completely shattered. The drop of oil in the dish also explodes violently when touched with a feather dipped in turpentine. This experiment should be tried in the open air, and with adequate precautions, only by an experienced chemist.

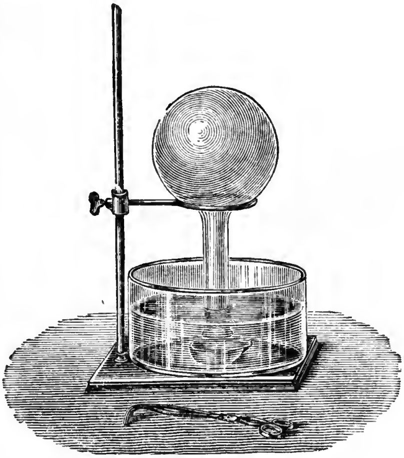


FIG. 290.—Preparation of Nitrogen Trichloride.

EXPT. 216.—The formation of nitrogen chloride may be safely shown by the apparatus of Fig. 291. The solution of ammonium chloride saturated at 28° is poured into the tube, closed at the lower end with a piece of moist bladder, and the whole dipped into a trough of the solution. Electrodes of platinum foil are immersed in the tube and dish, and a layer of turpentine is poured over the solution in the tube. The electrode *in the tube* is made the anode. As each drop of trichloride rises and enters the turpentine it explodes, forming nitrogen and chlorine.

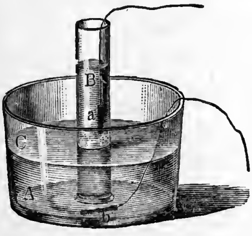


FIG. 291.—Demonstration of Explosion of NCl_3.

Gattermann found that the trichloride had the formula NCl_3

if the action of chlorine was prolonged, but the chlorination of ammonia proceeds in three stages:

$$NH_3 + Cl_2 = NH_2Cl \text{ (monochloramine)} + HCl;$$
$$NH_2Cl + Cl_2 = NHCl_2 \text{ (dichloramine)} + HCl;$$
$$NHCl_2 + Cl_2 = NCl_3 \text{ (trichloramine)} + HCl.$$

The analysis was carried out by decomposing with ammonia: $NCl_3 + 4NH_3 = N_2 + 3NH_4Cl$, and precipitating the chloride with silver nitrate. The percentage of chlorine was found to be 89·1; NCl_3 requires 89·17.

Monochloroamine, NH_2Cl, is formed as an unstable yellow liquid when ammonia and sodium hypochlorite are mixed in equimolecular proportions and the liquid is distilled in a vacuum: $NaOCl + NH_3 = NaOH + NH_2Cl$. By the action of nitrogen trichloride on potassium bromide, Millon obtained a dark red, volatile, explosive oil, possibly **nitrogen tribromide.**

Nitrogen iodide.—By the action of iodine on a solution of ammonia, Courtois (1829) obtained a black explosive powder. This was examined by Gladstone (1855), who gave it the formula NHI_2, whilst Stahlschmidt (1863) considered it to be NI_3. Bunsen (1852), by mixing alcoholic solutions of iodine and ammonia, obtained $N_2I_3H_3$, *i.e.*, $NI_3{\cdot}NH_3$. Szuhay (1893), by suspending the black "iodide of nitrogen" in water and adding silver nitrate, obtained a black explosive powder, which he stated to have the composition $NAgI_2$. The formula NHI_2 was therefore considered to be correct. Chattaway and Orton (1900) found, however, that the first product of the action of iodine on aqueous ammonia is a dark red crystalline compound, $NI_3{\cdot}NH_3$, and they confirmed the observation of Selivanoff (1894) that hypoiodous acid is the first product of the reaction. This appears to react with more ammonia to form the iodide of nitrogen, possibly by decomposition of ammonium hypoiodite: (*a*) $NH_4{\cdot}OH + I_2 = NH_4I + HOI$; (*b*) $NH_3 + HOI = NH_4OI$; (*c*) $3NH_4OI \rightleftharpoons N_2H_3I_3 + NH_4{\cdot}OH + 2H_2O$.

If iodide of nitrogen is treated with sodium sulphite it is decomposed: $N_2H_3I_3 + 3Na_2SO_3 + 3H_2O = 2Na_2SO_4 + 2NH_4I + HI$. The free acid may be titrated with baryta, and the iodide with silver nitrate, and the composition of the substance so determined. Silberrad (1905) confirmed the formula by the action of zinc ethyl on the substance:

$$N_2H_3I_3 + 3Zn(C_2H_5)_2 = 3ZnC_2H_5I + NH_3 + N(C_2H_5)_3.$$

He showed that Szuhay's compound is $NI_3{\cdot}AgNH_2$.

Expt. 217.—If a dilute solution of iodine is added drop by drop to a solution of ammonia, the liquid at first remains clear, and gives the reactions of hypoiodous acid (*e.g.*, a brown precipitate with $MnSO_4$).

On further addition of iodine, a black precipitate of iodide of nitrogen is formed. If a large amount of concentrated ammonia is added, this redissolves, showing that reaction (*c*) above is reversible.

Expt. 218.—Triturate 1 gm. of iodine with concentrated ammonia. A black powder is formed, which is filtered off. The iodide of nitrogen is fairly stable when moist. The filter-paper is torn into a number of pieces, which are allowed to dry spontaneously. If one portion is touched with a feather, it explodes—sometimes spontaneous explosion occurs. If the other portions are not kept at a distance they also explode. If two portions are placed close together, and one is exploded, the shock brings about the explosion of the other portion. Violet fumes of iodine are evolved. If one of the portions of the *moist* substance is placed in water and exposed to light, bubbles of nitrogen are evolved. Another portion of the moist iodide may be dissolved in concentrated ammonia, when a brown solution containing iodine and ammonium iodate is formed on warming.

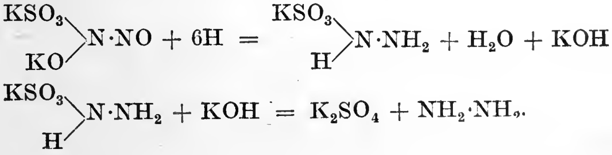
Nitrogen iodide is an active oxidising agent, oxidising sulphites to sulphates, arsenious acid into arsenic acid, etc. Each atom of iodine has an oxidising effect of an atom of oxygen, as in hypoiodous acid, HOI.

Hydrazine, N_2H_4.—Hydrazine, or **diamide,** N_2H_4, was prepared by Curtius in 1887 from organic compounds. Raschig obtained it by the action of sodium hypochlorite on ammonia solution in the presence of a little glue. Monochloroamine is first formed, which then reacts with ammonia to form hydrazine :

$$\begin{aligned} NH_3 + NaOCl &= NH_2Cl + NaOH \\ NH_3 + NH_2Cl &= NH_2{\cdot}NH_2 + HCl. \end{aligned}$$

Expt. 219.—One litre of commercial sodium hypochlorite solution is mixed with 12 c.c. of a 5 per cent. solution of glue and added to 3 litres of concentrated ammonia. The solution is concentrated by evaporation to drive off excess of ammonia, and neutralised with sulphuric acid. On cooling, 80–90 gm. of **hydrazine sulphate,** N_2H_4,H_2SO_4, are obtained.

Hydrazine is also formed by the reduction of **potassium nitroso-hydroxylamine sulphonate,** obtained by saturating a solution of potassium nitrite with sulphur dioxide. This salt, which has the empirical formula $K_2SO_3{\cdot}N_2O_2$, is suspended in ice-cold water and treated with sodium amalgam :



$$\left.\begin{matrix}KSO_3\\KO\end{matrix}\right\rangle N{\cdot}NO + 6H = \left.\begin{matrix}KSO_3\\H\end{matrix}\right\rangle N{\cdot}NH_2 + H_2O + KOH$$

$$\left.\begin{matrix}KSO_3\\H\end{matrix}\right\rangle N{\cdot}NH_2 + KOH = K_2SO_4 + NH_2{\cdot}NH_2.$$

If hydrazine sulphate is distilled under reduced pressure with concentrated potash solution, with a condenser without rubber or cork connections, a colourless fuming liquid, b.-pt. 119°, or 47°/26 mm., is obtained. This is called **hydyazine hydrate,** N_2H_4,H_2O, but appears to be a solution of maximum boiling point (p. 237). If the hydrate is distilled with its own weight of caustic soda in small pieces, **anhydrous hydrazine** passes over at 150° as a liquid which solidifies on cooling into colourless crystals, m.-pt. 1·4°, b.-pt. 113·5°. Anhydrous hydrazine may also be prepared from the hydrochloride and sodium methoxide (p. 553). Hydrazine, and the hydrate, readily absorb moisture and carbon dioxide from the air, are freely soluble in water and alcohol, and are poisonous. Anhydrous hydrazine inflames in dry oxygen, reacts readily with halogens: $2I_2 + N_2H_4 = 4HI + N_2$, explodes in contact with potassium permanganate, sets free ammonia from ammonium chloride, and decomposes on heating: $3N_2H_4 = N_2 + 4NH_3$.

Hydrazine in solution acts as a very weak base: it forms two series of salts, *e.g.*, N_2H_4,HCl, $N_2H_4,2HCl$; $2N_2H_4,H_2SO_4$, N_2H_4,H_2SO_4. The ordinary **hydrazine sulphate** is N_2H_4,H_2SO_4, or $(N_2H_6)HSO_4$. The salts are ionised and hydrolysed in solution: $N_2H_4,2HX \rightleftharpoons N_2H_4,HX + HX \rightleftharpoons N_2H_5^{\cdot} + H^{\cdot} + 2X'$. Double salts, *e.g.*, $ZnCl_2,N_2H_4,2HCl$, are known.

Hydrazine and its salts are the most powerful **reducing agents** known, precipitating gold, silver, and platinum from their salts, reducing alkaline copper solutions to cuprous oxide: $4CuO + N_2H_4 = 2Cu_2O + 2H_2O + N_2$; ferric salts to ferrous salts, and iodates to iodides: $3N_2H_4,H_2SO_4 + 2KIO_3 = 2HI + 2KHSO_4 + H_2SO_4 + 6H_2O + 3N_2$. Hydrazine may be estimated by titration with iodine in presence of sodium bicarbonate: $N_2H_4 + 2I_2 = N_2 + 4HI$, or with potassium permanganate in presence of dilute sulphuric acid: $N_2H_4 + 2O = N_2 + 2H_2O$.

Hydrazoic acid, HN_3.—Hydrazoic acid, or **azoimide,** HN_3, was obtained by Curtius in 1890 from organic compounds. It is formed by the careful oxidation of hydrazine with nitric acid or hydrogen peroxide: $3N_2H_4 + 3O = 2HN_3 + 3H_2O$.

EXPT. 220.—Warm 1 gm. of hydrazine sulphate with 4 c.c. of HNO_3 of sp. gr. 1·3 in a test-tube, and lead the vapours into a solution of silver nitrate. A white, curdy precipitate of **silver azide,** AgN_3, is formed. This compound is explosive when dry. It is soluble in ammonia (*cf.* AgCl).

Hydrazoic acid is also formed by the decomposition of hydrazine nitrite under special conditions:

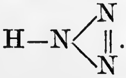
$$N_2H_4,HNO_2 = HN_3 + 2H_2O$$
$$(cf.\ NH_3,HNO_2 = N_2 + 2H_2O).$$

If hydrazine is treated with ethyl or amyl nitrite and alkali, sodium azide is formed, and a precipitate of silver azide is produced when hydrazine is added to a concentrated solution of silver nitrite.

Wislicenus (1892) first prepared hydrazoic acid from inorganic materials. Sodamide, $NaNH_2$, is prepared by passing dry ammonia over pieces of sodium in porcelain boats in a hard glass tube heated to 150–250° : $2Na + 2NH_3 = 2NaNH_2 + H_2$. The ammonia is then displaced by a current of dry nitrous oxide, and the tube heated to 190°. The sodamide swells up, and ammonia is evolved : (*a*) $NaNH_2 + N_2O = NaN_3 + H_2O$; (*b*) $NaNH_2 + H_2O = NaOH + NH_3$. When no more ammonia is evolved, the tube is cooled, and the pumice-like mass of NaN_3 and NaOH distilled with dilute sulphuric acid, when a solution of hydrazoic acid, HN_3, comes over.

The solution is fractionated, and finally distilled with fused calcium chloride, when anhydrous hydrazoic acid is formed. This is a colourless mobile liquid, b.-pt. 37°, m.-pt. $-80°$, with a nauseous smell. It is dangerously explosive. It dissolves readily in water, forming a corrosive acid liquid, in which about 1 per cent. of the acid is ionised : $HN_3 \rightleftharpoons H^{\cdot} + N_3'$. The solution readily dissolves iron, zinc, copper, and aluminium, with evolution of hydrogen and ammonia : $2HN_3 + Zn = Zn(N_3)_2 + H_2$; $HN_3 + 6H = NH_3 + N_2H_4$.

The salts give a blood-red colour with ferric chloride, resembling thiocyanates ; with silver nitrate they give a white, curdy precipitate of silver azide, AgN_3, soluble in ammonia, and exploding at 250°. By neutralising the acid with ammonia and hydrazine, respectively, the salts $NH_4N_3(N_4H_4)$ and $N_2H_4{\cdot}HN_3(N_5H_5)$ are obtained in colourless explosive crystals.

The constitutional formula of hydrazoic acid was formerly written as : . Thiele represents it as N⋮N:NH, which agrees with the formation of NH_3 and N_2H_4 on reduction. The group N_3 is a *negative group* (*cf.* p. 517), whilst NH_2 is a *positive group* ; $H—NH_2$ is a base.

EXERCISES ON CHAPTER XXVIII

1. How is nitrogen obtained : (*a*) from air, (*b*) from ammonia, (*c*) from ammonium nitrite ? How do these varieties of nitrogen differ from one another, and what is the cause of the difference ?

2. How is pure nitrogen obtained ? What are its physical and chemical properties?

3. With what substances, and under what conditions, does nitrogen

unite directly ? How may ammonia be prepared from atmospheric nitrogen ?

4. What are the sources of commercial ammonia ? A specimen of ammonia contains ammonium sulphide: how would you prepare pure ammonia from it ?

5. How is ammonia made: (*a*) in the laboratory; (*b*) on the large scale ? Describe the principal properties of the gas.

6. How is the composition of ammonia determined ? Twenty c.c. of a mixture of ammonia and nitrogen are exploded with oxygen. The contraction is 7·5 c.c. What volumes of the gases are present in the mixture ?

7. How is ammonium sulphate obtained on the large scale ?

8. How are hydroxylamine salts obtained ? How is hydroxylamine obtained from its salts ?

9. What are the principal properties of hydroxylamine ? Describe reactions in which it functions: (*a*) as a base; (*b*) as a reducing agent; (*c*) as an oxidising agent.

10. How is hydrazine sulphate obtained ? Starting with this salt, how would you prepare anhydrous hydrazine ? Describe the properties of these substances.

11. What halogen compounds of nitrogen are known ? Describe briefly their preparation and properties.

12. How is hydrazoic acid obtained ? What are the properties of this substance ?

13. What is the action of ammonia on: (*a*) chlorine, (*b*) potassium, (*c*) nitrous acid, (*d*) oxygen ?

CHAPTER XXIX

THE OXIDES AND OXY-ACIDS OF NITROGEN

Oxides and oxy-acids of nitrogen.—A number of oxides and oxy-acids of nitrogen are known : the following table may be compared with that of the oxy-compounds of chlorine (p. 373) :

Nitrous oxide, N_2O → **Hyponitrous acid** $(N\cdot OH)_2$ or $H_2N_2O_2$
Nitric oxide, NO → **Nitrohydroxylamic acid,** $HON{:}NO_2H$
Nitrogen trioxide, or Nitrous anhydride N_2O_3 → **Nitrous acid,** HNO_2
Nitrogen dioxide, or tetroxide, NO_2, N_2O_4 ↗ ↘
Nitrogen pentoxide, or nitric anhydride, N_2O_5 → **Nitric acid,** HNO_3
Nitrogen heptoxide, N_2O_7 (?) → **Pernitric acid,** HNO_4 (?)

In many of its oxy-compounds nitrogen is quinquevalent.

TYPE NX_3.	TYPE NX_5.
$\mathbf{NH_3}$, **ammonia**	NH_4 ; $\mathbf{NH_4Cl}$, **ammonium chloride**
$\mathbf{NH_2(OH)}$, **hydroxylamine**	$\mathbf{NH_4\cdot OH}$, **ammonium hydroxide**
$NH(OH)_2$, dihydroxyammonia, or dihydroxylamine	$NH_3(OH)_2$
$N(OH)_3$, orthonitrous acid	$NH_2(OH)_3$
Dehydration products :—	$NH(OH)_4$
$NH(OH)_2 - H_2O \rightarrow N\cdot OH$	$N(OH)_5$, orthonitric acid
Nitrous oxide ↓ $\mathbf{N_2O} + H_2O \leftarrow (\mathbf{N\cdot OH})_2$ **hyponitrous acid**	**Dehydration products :—** $NR_3(OH)_2 - H_2O \rightarrow \mathbf{ONR_3}$, **oxy-amines**
$N(OH)_3 - H_2O \rightarrow \mathbf{NO\cdot OH}$, **nitrous acid**	$NR(OH)_4 - 2H_2O \rightarrow \mathbf{R\cdot NO_2}$, **nitro-compounds**
$2NO\cdot OH - H_2O \rightarrow N_2O_3$, **nitrous anhydride**	$N(OH)_5 - H_2O \rightarrow NO\cdot(OH)_3$, meso-nitric acid
	$NO(OH)_3 - H_2O \rightarrow NO_2\cdot OH$, **nitric acid** (meta)
	$2NO_2\cdot OH - H_2O \rightarrow \mathbf{NO_2\cdot O\cdot NO_2}$ or $\mathbf{N_2O_5}$, **nitric anhydride**
	Dehydration products :—
Hydrazine, $\mathbf{H_2N\cdot NH_2}$ →	$(HO)_2NH\cdot N(OH)_3 - 2H_2O \rightarrow$ $\mathbf{HON{:}NO_2H}$, **nitrohydroxylamic acid**
	$\mathbf{HON{:}NO_2H} - H_2O \rightarrow 2\mathbf{NO}$, **nitric oxide.**

Compounds in heavy type are known; others are hypothetical. R indicates an organic radical, *e.g.*, ethyl, C_2H_5—.

The union of nitrogen and oxygen.—Nitrogen and oxygen combine directly at high temperatures to form **nitric oxide**: $N_2 + O_2 \rightleftharpoons 2NO$. With excess of oxygen this forms on cooling red fumes of **nitrogen dioxide**: $2NO + O_2 = 2NO_2$. If water is present as well as excess of oxygen, the nitrogen dioxide dissolves, forming a solution of **nitrous** and **nitric acids**: $2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3$. Nitrous acid is unstable, the solution becoming pale blue in colour owing to the formation of **nitrous anhydride**, N_2O_3. This also decomposes, forming nitrogen dioxide and nitric oxide, which are evolved: $N_2O_3 \rightleftharpoons NO_2 + NO$. The nitric oxide is again oxidised, and finally all the oxides of nitrogen are converted into dilute nitric acid.

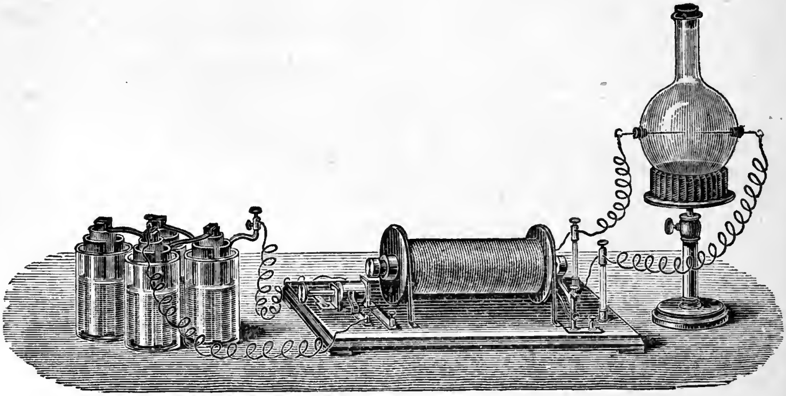


FIG. 292.—Combination of Nitrogen and Oxygen by Sparking.

EXPT. 221.—Pass a series of sparks through air in a globe (Fig. 292). After a time the gas becomes yellowish in colour, and if it is shaken with litmus solution the latter is turned red. This observation was first made by Priestley (1779).

Nitric acid is also formed when a mixture of detonating gas (2 vols. of H_2 + 1 vol. of O_2) with air is exploded by a spark. If the volume of air is more than double that of the detonating gas, the temperature of explosion is too low to lead to the formation of nitric acid. Thus, no acid is formed on exploding a mixture of hydrogen and air. This observation is due to Cavendish (1781).

If nitric acid is distilled with phosphorus pentoxide, **nitric anhydride** is formed: $2HNO_3 = N_2O_5 + H_2O$. By the action of dilute nitric acid on zinc, or by heating ammonium nitrate, **nitrous oxide** is obtained: $NH_4NO_3 = N_2O + 2H_2O$.

Nitre or saltpetre.—If soil containing decomposing nitrogenous organic matter, such as urine, is mixed with lime or calcium carbonate, such as old mortar, **calcium nitrate,** $Ca(NO_3)_2$, is produced. It probably arises from the oxidation of ammonia, formed by the decomposition of organic matter, in the presence of feeble alkalies, by the activity of micro-organisms, known as **nitrifying bacteria,** present in all fertile soil. If an infusion of soil is added to a dilute solution of an ammonium salt containing calcium carbonate in suspension, calcium nitrate is formed. The first product of oxidation may be calcium nitrite, which is then fully oxidised to nitrate, and two kinds of bacteria are usually involved:

$$NH_3 \xrightarrow{+3O} HNO_2 \xrightarrow{+O} HNO_3.$$

There are, however, bacteria which convert ammonium salts directly into nitrates. If the material is lixiviated, a solution containing calcium nitrate is obtained, which is boiled with wood-ashes (containing potassium carbonate): $Ca(NO_3)_2 + K_2CO_3 = CaCO_3 + 2KNO_3$. The filtrate on evaporation deposits prismatic crystals of **nitre, saltpetre,** or **potassium nitrate,** KNO_3.

This method of obtaining nitre by means of **nitre plantations** is still used in India, where about 20,000 tons are made annually.

Potassium nitrate usually crystallises in large rhombic prisms, but if the solution is slowly evaporated on a watch-glass, rhombohedra, isomorphous with sodium nitrate, deposit. The rhombic form is stable below 129°, a second rhombohedral form at higher temperatures. Nitre melts at 339°, and the fused salt is a powerful oxidising agent. Sulphur, charcoal, and phosphorus take fire in it, and burn brilliantly, with formation of potassium sulphate, carbonate, and phosphate. This property is applied in the manufacture of **gunpowder.**

Potassium nitrate is used in pickling meat, to which it imparts a bright red colour (*e.g.*, hams), and in medicine. It is used as a fertiliser, since both potassium and nitrates are essential to the growth of plants (p. 696).

Sodium nitrate; Chile nitre, $NaNO_3$.—In 1830 the existence of extensive deposits of **sodium nitrate,** $NaNO_3$, was discovered in the rainless districts of Chile. The zone of nitrates appears to cover 77,000 square miles,of which less than 3 per cent. is explored and prospected. In the surveyed area the supply is 240,000,000, tons, estimated, with normal production, as sufficient for one hundred years. Other authorities give three hundred years as the probable period of exhaustion of the nitre beds. The exports of sodium nitrate from Chile have been as follows :

Year.	Export in tons.	Year.	Export in tons.
1830–34 ..	16,780	1890	1,000,000
1865	491,100	1895	1,267,000
1875	334,000	1905	1,705,000
1885	512,600	1915	2,090,000

The sodium nitrate in the deposits constitutes from 20 to 50 per cent. in a distinct stratum of earth known as *caliche,* resting upon soft clay, and covered with a compact top layer called *costra,* containing less nitrate. The surface soil having been removed, holes are bored through the costra into the caliche, charges of slow-burning powder are inserted and tamped, and the caliche is then broken up by the explosion. The pieces of caliche are conveyed to the lixiviation works, known as *officina,* where the material is crushed and lixiviated in large tanks of water heated by steam. The settled solution is run off to crystallisers, where crude nitrate separates, the mother liquors being run back to the lixiviators. The crystals are washed with a little water and dried in the sun : they contain 95–96 per cent. of $NaNO_3$, and are exported in bags.

About four-fifths of the export of Chile nitre is used directly as a **fertiliser:** the remainder is used as a source of **nitric acid,** for the manufacture of explosives, dyes, and drugs.

Sodium nitrate crystallises in rhombohedra resembling cubes, hence it is sometimes called "cubic nitre." It differs from potassium nitrate in being deliquescent ; it fuses at 316°, and at higher temperatures evolves oxygen, leaving nitrite : $2NaNO_3 = 2NaNO_2 + O_2$.

Sodium nitrate is converted into potassium nitrate by dissolving potassium chloride in hot water till the sp. gr. is 1·2, and then adding sodium nitrate till the sp. gr. rises to 1·5. Sodium chloride, the least soluble salt formed from the four ions, is deposited from the hot liquid, since its solubility is not appreciably increased by rise of temperature ; if the mother liquor is allowed to cool, potassium nitrate crystallises out, since it is the least soluble salt at lower temperatures : $NaNO_3 + KCl \rightleftharpoons KNO_3 + NaCl$. It is recrystallised from water.

Gunpowder.—Most of the potassium nitrate of commerce is used in making **gunpowder.** This was apparently first made by the Chinese for the production of fireworks. *Greek fire* was a mixture of nitre, pitch, and sulphur. The invention of gunpowder is usually credited to Roger Bacon (1214-1294), although it is explicitly described by Marcus Graecus (eighth century), who also gives recipes for "liquid fire" for military purposes. Gunpowder was first used by the English, in the battle of Crécy, in 1346. It consists of a mixture of finely-powdered nitre, wood-charcoal (carbonised at a low temperature), and sulphur, usually in the proportions 74·9 : 13·3 : 11·8, the materials being ground and incorporated under stone rollers. (Marcus Graecus gives 60 : 20 : 10.) The proportions of the constituents, and the main products of combustion, correspond roughly with the following equation: $2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2$.

Carbon monoxide, however, is also evolved, and the residue contains potassium carbonate and sulphate. Abel and Noble (1875) found that the explosion of gunpowder cannot adequately be represented by a chemical equation, since the reactions are exceedingly complicated.

The equation given shows that $(2 \times 101 + 32 + 3 \times 12) = 270$ gm. of powder produce $4 \times 22{\cdot}3$ litres of gas at S.T.P. The solid powder occupies about 100 c.c., hence the expansion at S.T.P. will be about 800. The temperature of the gaseous products, at the instant of explosion, is about 2000°, so that the theoretical liberation of energy in firing 1 gm. of powder should be about

$$\frac{(4 \times 22300 - 100)}{270} \times \frac{2273}{273} \times 1033 = 2{\cdot}84 \times 10^6 \text{ gm. cm.},$$

or $2{\cdot}8 \times 10^9$ ergs. This would impart to a bullet of mass 1 gm. a muzzle velocity of $\sqrt{2 \times 2{\cdot}8 \times 10^9} = 7{\cdot}5 \times 10^4$ cm. per sec.

Nitric acid, HNO_3.—The Latin Geber describes the preparation of *aqua fortis* by distilling nitre with alum and copper sulphate: "Take a pound of vitriol of Cyprus, a pound and a half of saltpetre, a quarter of alum of Jameni; submit the whole to distillation in order to obtain a liquid which has great solvent power" ("Alchimiae Geberi," 1529). Glauber (1603–1668) obtained a more concentrated fuming acid by distilling nitre with oil of vitriol ("Philosophische Oefen," 1648). The acid was therefore known as *spiritus nitri fumans Glauberi*. The presence of oxygen in nitric acid was demonstrated by Lavoisier in 1776.

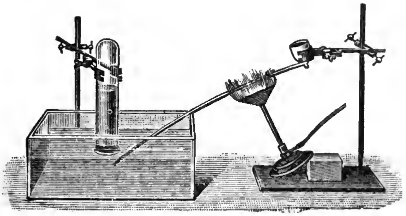


FIG. 293.—Decomposition of Nitric Acid by Heat.

EXPT. 222.—Arrange a clay tobacco pipe as shown in Fig. 293. Heat one part of the stem strongly with a Bunsen burner, and pour 5 c.c. of concentrated nitric acid into the bowl. The acid is decomposed on passing through the hot tube, and bubbles of oxygen collect in the test-tube.

The composition of nitric acid was elucidated by Cavendish (1784). He passed a series of sparks through a mixture of oxygen and nitrogen confined over mercury and potash solution in an inverted U-tube (Fig. 294). The gas gradually disappeared, with the exception of a very small bubble (p. 600), and a solution of nitre was formed. Thus, nitric acid is formed from oxygen and nitrogen in the presence of water.

Cavendish says: "We may safely conclude that in the present experiments the phlogisticated air [N] was enabled, by means of the electric spark, to unite to, or form a chemical combination with, the dephlogisticated air [O], and was thereby reduced to nitrous [nitric] acid, which united with the soap-lees [potash] and formed a solution of nitre; for in these experiments those two airs actually disappeared, and nitrous acid was formed in their room."

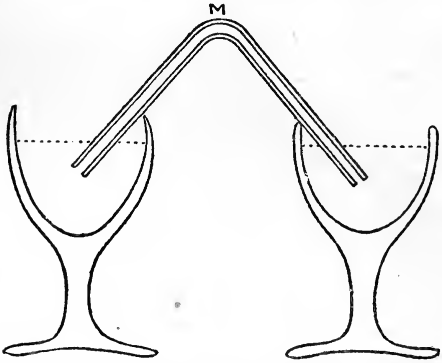


FIG. 294.—Cavendish's Apparatus for Sparking Air over Potash Solution.

Nitric acid is prepared in the laboratory by distilling potassium or sodium nitrate with concentrated sulphuric acid: $KNO_3 + H_2SO_4 \rightleftharpoons KHSO_4 + HNO_3$. If excess of nitre is used, and a high temperature, further decomposition occurs, the acid sulphate being converted into normal sulphate:

$$KHSO_4 + KNO_3 = K_2SO_4 + HNO_3.$$

A glass retort is then usually cracked, and part of the acid is decomposed, with production of red fumes of oxides of nitrogen: $4HNO_3 \rightleftharpoons 4NO_2 + 2H_2O + O_2$. These fumes dissolve in the acid, colouring it yellow.

EXPT. 223.—Add 49 gm. of concentrated sulphuric acid to 50 gm. of potassium nitrate in a stoppered retort. Heat on wire gauze, and collect the nitric acid in a cooled receiver (Fig. 295). Notice the red fumes at the beginning and end of the process. The residue in the retort may be poured out into a porcelain dish, and solidifies to a white crystalline mass of impure **potassium hydrogen sulphate,** $KHSO_4$. If a little of this is powdered, mixed with powdered KNO_3, and heated in a test-tube, white fumes of nitric acid and red fumes of NO_2 are evolved. A glowing chip inflames in the gas, showing that oxygen is also produced.

Pure nitric acid is obtained by redistilling on a water-bath under reduced pressure, and passing ozonised oxygen through the distillate. It is a colourless liquid of sp. gr. 1·52. The pure acid may also be obtained by freezing 98 per cent. acid, when colourless crystals, m.-pt. – 41·3°, separate.

The liquid acid and the vapour are slightly dissociated at the ordinary temperature: $2HNO_3 \rightleftarrows N_2O_5 + H_2O$, and the dissociation increases with the temperature. Anhydrous HNO_3 does not exist in the liquid state. If a current of dry air is passed through the liquid acid, the more volatile nitric anhydride is removed, and an acid of constant boiling point (about 86°) containing 98·62 per cent. of HNO_3, is obtained. The acid decomposes on distillation under atmospheric pressure. It begins to boil at 78·2°, with decomposition. When three-fourths of the acid has distilled over, the residue contains 95·8 per cent. of HNO_3; with further distillation an acid of maximum boiling point (120·5°), containing 68 per cent. of HNO_3, is formed. This is also formed when weaker solutions are distilled. This acid, although it corresponds approximately with $2HNO_3,3H_2O$, is not a definite hydrate; Roscoe showed that, as in the case of hydrochloric acid, the composition of the distillate is a function of the pressure. Two solid **hydrates,** HNO_3,H_2O (m.-pt. – 38°) and $HNO_3,3H_2O$ (m.-pt. – 18·5°), are known.

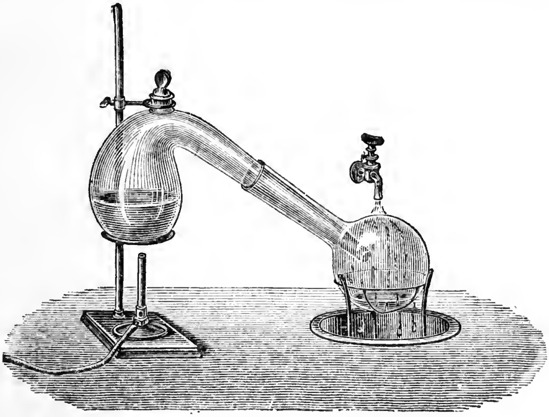


FIG. 295.—Preparation of Nitric Acid.

Nitric acid vapour is decomposed by light. If a bottle half filled with acid is exposed to light, the nitrogen dioxide formed dissolves in the liquid and renders it yellow. The liquid in a completely filled bottle remains colourless. The yellow acid may be rendered colourless by warming to 60–80°, and bubbling dry air through it;

or by adding a little lead dioxide, when oxides of nitrogen are converted into lead nitrate, which is insoluble in the concentrated acid, and separates with the excess of dioxide : $PbO_2 + N_2O_4 = Pb(NO_3)_2$.

A yellow, so-called **fuming nitric acid,** containing oxides of nitrogen, is used as an oxidising agent, and is prepared by distilling nitre and sulphuric acid with a little starch. The starch reduces a portion of the nitric acid to N_2O_3 and N_2O_4, which dissolve in the acid.

Heat is evolved, and contraction occurs, when concentrated nitric acid and water are mixed. The maximum effect occurs with the mixture $3HNO_3 + H_2O$, although no definite hydrate of this composition has been isolated.

The **densities** of mixtures of nitric acid and water at 15° are given in the table below.

Density.	Per cent. HNO_3	Density.	Per cent. HNO_3	Density.	Per cent. HNO_3
1·050	8·99	1·250	39·82	1·450	77·28
1·100	17·11	1·300	47·49	1·500	94·09
1·150	24·84	1·350	55·79	1·510	98·10
1·200	32·36	1·400	65·30	1·520	99·67

Chemical properties of nitric acid.—Nitric acid is a **strong acid,** and is largely ionised in solution : $HNO_3 \rightleftharpoons H^{\cdot} + NO_3'$. It is monobasic, and forms only one series of salts, the **nitrates,** which are obtained by the action of nitric acid on the metals, when oxides of nitrogen and not hydrogen are usually evolved (p. 570), on the oxides or hydroxides, or on the carbonates.

EXPT. 224.—Dissolve copper turnings in dilute nitric acid. Observe that red fumes are evolved. Evaporate the blue solution, and allow to cool. Blue deliquescent crystals of **cupric nitrate,** $Cu(NO_3)_2,3H_2O$, are obtained.

EXPT. 225.—Neutralise a solution of caustic potash with dilute nitric acid, evaporate, and allow to cool. Prismatic crystals of **nitre,** KNO_3, separate.

EXPT. 226.—Dissolve lead carbonate in warm dilute nitric acid, filter from excess of carbonate, and evaporate. Octahedral crystals of **lead nitrate,** $Pb(NO_3)_2$, are formed.

Nitric acid also acts as an **oxidising agent.** Concentrated nitric acid, when boiled with iodine, oxidises the halogen to iodic acid, HIO_3. Phosphorus is oxidised to phosphoric acid, sulphur to sulphuric acid, arsenious oxide to arsenic acid. Tin is oxidised by concentrated nitric acid in the cold, with evolution of red fumes, and a white residue of hydrated stannic oxide remains. Burning charcoal burns brilliantly in the concentrated acid, and heated sawdust is inflamed.

Expt. 227.—Heat a little sawdust on a sand-bath until it begins to char, and pour over it *a few drops* of fuming nitric acid from a test-tube. The sawdust burns.

Oil of turpentine explodes with concentrated nitric acid, with evolution of black clouds of carbon. Alcohol is violently oxidised, with the production of a variety of substances, and usually with explosion.

Sulphuretted hydrogen is not oxidised by pure nitric acid, but in presence of nitrogen oxides it is decomposed with separation of sulphur. Stannous chloride in hydrochloric acid is oxidised to stannic chloride; the nitric acid is reduced to hydroxylamine and ammonia.

Ferrous salts reduce nitric acid to nitric oxide, NO, and this dissolves in the excess of ferrous salt to form a black solution, from which nitric oxide is expelled on heating. The first reaction is: $6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$. This is utilised as a **test** for nitric acid or nitrates. In the case of nitrates, concentrated sulphuric acid must be added before the colour appears.

Expt. 228.—Dissolve a few crystals of ferrous sulphate in a cold dilute solution of potassium nitrate in a test-tube, and pour pure concentrated sulphuric acid (the commercial acid contains oxides of nitrogen which give a black colour with ferrous sulphate) carefully into the liquid so as to form a heavy layer below. At the junction of the liquids a black ring (purple if only traces of nitrate are present) is formed. On shaking, the black colour disappears, bubbles of nitric oxide are evolved, and a yellow solution of ferric sulphate remains.

Other tests for nitric acid are: (i) the red colour produced with a solution of the alkaloid brucine in concentrated sulphuric acid; (ii) the deep blue colour with a solution of diphenylamine in concentrated sulphuric acid; (iii) the evolution of red fumes of oxides of nitrogen when heated with concentrated sulphuric acid and copper turnings.

Dilute nitric acid is used as an oxidising agent in organic chemistry. Thus, if toluene, $C_6H_5 \cdot CH_3$, is boiled with the dilute acid, it is oxidised to benzoic acid, $C_6H_5 \cdot COOH$.

Concentrated nitric acid, in the absence of water (*e.g.*, in presence of concentrated sulphuric acid), acts on many organic compounds so as to replace one or more atoms of hydrogen by the **nitro-group,** NO_2. This action is called **nitration,** and in it the acid behaves as though it had the structural formula $NO_2 \cdot OH$.

Thus, benzene is converted into **nitrobenzene**: $C_6H_6 + NO_2 \cdot OH = C_6H_5NO_2 + H_2O$; phenol yields, on prolonged nitration, trinitrophenol, or **picric acid**:

$$C_6H_5 \cdot OH + 3NO_2 \cdot OH = C_6H_2(NO_2)_3 \cdot OH + 3H_2O;$$

toluene forms **trinitrotoluene** (T.N.T), $C_6H_2(NO_2)_3{\cdot}CH_3$, which, like picric acid, is a powerful explosive.

EXPT. 229.—Shake a few drops of benzene with a mixture of concentrated nitric and sulphuric acids in a test-tube. Pour into water: a yellow oil (nitrobenzene), smelling of bitter almonds, separates.

Glycerin and cotton (cellulose) do not form nitro-compounds in the true sense, but salts of nitric acid with organic radicals, *i.e.*, **esters** of nitric acid. **Nitroglycerin** is really **glyceryl trinitrate:** $C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O$; **nitrocelluloses,** containing from four to six NO_3 groups according to the concentration of the acid, constitute *collodion* and *gun-cotton*; the former is soluble in a mixture of alcohol and ether: $C_{12}H_{20}O_{10} + 4HNO_3 = C_{12}H_{16}O_6(NO_3)_4 + 4H_2O$.

The action of nitric acid on metals.—All metals, except platinum, rhodium, iridium, and gold, are attacked by dilute or concentrated nitric acid. Tin, antimony, tungsten, molybdenum, and arsenic are converted into the oxides; the rest form nitrates. During the reaction a portion of the acid is reduced, with the formation of the oxides NO_2, N_2O_3, NO, and N_2O, free nitrogen, hydroxylamine, and ammonia. The products depend on the metal, the temperature, the concentration of the acid, and the presence of the products of reaction in the solution. Hydrogen is evolved only by the metal magnesium, acting on cold dilute nitric acid: $Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$.

H. E. Armstrong and Ackworth (1877) suggested that the **primary reaction** in *all* cases is the liberation of nascent hydrogen: I. $M + HNO_3 = MNO_3 + H$. On the ionic theory, this corresponds with the reaction: $M + H^{\cdot} = M^{\cdot} + H$. This nascent hydrogen, however, is in contact with nitric acid, which is easily reduced, and further reactions occur:

II. **Secondary reactions,** which probably proceed in definite stages:
(*a*) $HNO_3 + H_2 = HNO_2$ (nitrous acid) $+ H_2O$.
(*b*) $2HNO_3 + 4H_2 = H_2N_2O_2$ (hyponitrous acid) $+ 4H_2O$.
(*c*) $HNO_3 + 3H_2 = NH_3O$ (hydroxylamine) $+ 2H_2O$.
(*d*) $HNO_3 + 4H_2 = NH_3$ (ammonia) $+ 3H_2O$;

III. **Tertiary reactions,** in which the secondary products interact:
(1) by **decomposition,** giving simpler compounds:
(*a*) $3HNO_2 = HNO_3 + 2NO$ (nitric oxide) $+ H_2O$.
(*b*) $2HNO_2 = N_2O_3$ (nitrous anhydride) $+ H_2O$.
(*c*) $H_2N_2O_2 = N_2O$ (nitrous oxide) $+ H_2O$;
(2) by **double decomposition:**
(*a*) $HNO_2 + NH_3 = N_2$ (nitrogen) $+ 2H_2O$.
(*b*) $HNO_2 + NH_3O = N_2O + 2H_2O$.

The action of nitric acid on **copper,** on Armstrong's theory, would be represented as follows:

I. $3Cu + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2$.
II. $3H_2 + 3HNO_3 = 3HNO_2 + 3H_2O$.
III. $3HNO_2 = HNO_3 + 2NO + H_2O$.
∴ by addition: $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$.

The reaction with **zinc,** which gives nitrous oxide, can be represented as follows:

I. $Zn + 2HNO_3 = Zn(NO_3)_2 + H_2$.
II. (*a*) $HNO_3 + 3H_2 = NH_3O + 2H_2O$.
(*b*) $HNO_3 + H_2 = HNO_2 + H_2O$.
III. $NH_3O + HNO_2 = N_2O + 2H_2O$.

To obtain $4H_2$ we require $4Zn + 8HNO_3$, and $2HNO_3$ are reduced; hence: $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$.

According to Divers, some metals give nitric oxide, but no hydroxylamine or ammonia: *e.g.*, Ag, Cu, Bi, Hg; whilst other metals give NH_3, or NH_3O, and N_2O: *e.g.*, Fe, Al, K, Zn, Sn, Cd, Mg (also gives H_2). The product, however, depends on the concentration and temperature of the acid: thus concentrated nitric acid gives mainly nitrogen dioxide with copper: $Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$; and also on the accumulation of the salt in the solution, since by the prolonged action of dilute nitric acid on copper, nitrogen is evolved.

Veley (1891) showed that *pure* nitric acid, in the absence of nitrous acid, scarcely acts on copper, silver, bismuth, or mercury. Other metals react in the absence of nitrous acid, but more slowly than when it is present. Since nitrous acid is formed in the reaction, the speed of the latter increases as it proceeds.

EXPT. 230.—Take three pieces of clean copper foil and immerse them in three glasses containing: (*a*) 50 c.c. of 50 per cent. nitric acid; (*b*) 50 c.c. of this nitric acid + 5 c.c. of hydrogen peroxide (20 vols.); (*c*) 50 c.c. of nitric acid + 1 gm. of urea. The foil in (*a*) is at once violently attacked; those in (*b*) and (*c*) remain for a time without change. The hydrogen peroxide oxidises nitrous acid: $HNO_2 + H_2O_2 = HNO_3 + H_2O$; whilst urea decomposes it: $CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O$.

According to Veley, nitric oxide is a primary product, formed from traces of nitrous acid; a green solution of copper nitrite is formed, which is then decomposed by nitric acid to reproduce nitrous acid, most of which decomposes:

I. $Cu + 4HNO_2 = Cu(NO_2)_2 + 2H_2O + 2NO$.
II. (*a*) $Cu(NO_2)_2 + 2HNO_3 = Cu(NO_3)_2 + 2HNO_2$;
(*b*) $3HNO_2 \rightleftharpoons HNO_3 + H_2O + 2NO$.

The manufacture of nitric acid.—Nitric acid is made on the large scale by three processes :

(1) The distillation of sodium nitrate with concentrated sulphuric acid : $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$; the **retort process.**

(2) The direct combination of nitrogen and oxygen of atmospheric air at the high temperature of the electric arc, and the subsequent oxidation of the nitric oxide to nitric acid in presence of excess of air and water :

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$4NO + 3O_2 + 2H_2O = 4HNO_3;$$ the **arc process.**

(3) The **oxidation of ammonia,** by passing a mixture of ammonia gas and air over a catalyst, such as heated platinum, and the subsequent treatment of the nitric oxide as in (2) :

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$
$$4NO + 3O_2 + 2H_2O = 4HNO_3.$$

Retort processes.—One or two tons of previously dried sodium nitrate (Chile nitre) are heated with rather more than this weight of concentrated sulphuric acid (93 per cent. H_2SO_4) in a large cast-iron pot, made in two or three pieces clamped together with asbestos packing and built in a brickwork furnace so as to allow of very uniform heating (Fig. 296). Nitric acid *vapour* does not attack iron, which is corroded by the liquid acid. At the top of the retort is a manhole for introducing the charge, and an outlet for the acid vapour, which is prolonged in a stoneware, silicon-iron, or vitrified silica pipe, in which there is a "lantern," consisting of a stoneware box with glass windows, or a short length of glass pipe, for observation. Twenty parts of coal

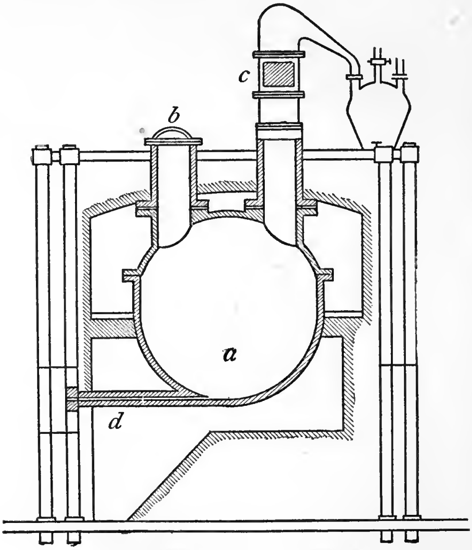


FIG. 296.—Nitric Acid Retort.

per 100 of nitre are required, and the distillation occupies about fifteen hours.

The acid is condensed in some type of cooler: various forms are used, consisting of vitrified silica spirals cooled in water, stoneware **U**-tubes or horizontal glass tubes cooled partly by air and water, or **S**-shaped tubes of silicon iron. Large stoneware Woulfe's bottles are also used. One type of condenser (Fig. 297) consists of earthenware tubes cooled by a shower of water. The red fumes of oxides of nitrogen also produced are condensed by water in a stoneware tower at the end, packed with hollow stoneware balls: $4NO_2 + 3O_2 + 2H_2O = 4HNO_3$.

In the **Valentiner process** (1891) the whole apparatus is air-tight, and a vacuum is maintained at the end by an air-pump. The distillation under reduced pressure (25 mm.) takes place at a lower temperature (100°), so that there is less decomposition, and the reaction also occurs more rapidly than in the ordinary process.

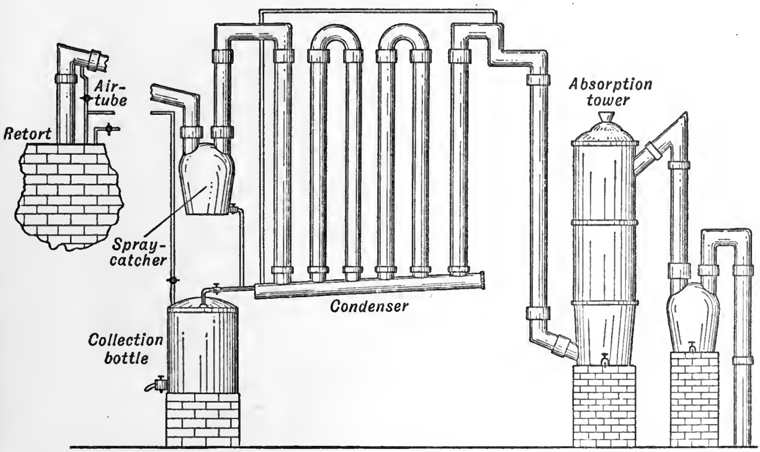


FIG. 297.—Guttmann Nitric Acid Plant.

The liquid residue in the retort is run out from the lower pipe, and allowed to solidify; it is a mixture or compound of $NaHSO_4$ and Na_2SO_4, with a little $NaNO_3$, and is called *nitre cake*.

The arc process.—The union of atmospheric nitrogen and oxygen at the high temperature of the electric arc was demonstrated by Crookes; a small experimental plant was worked at Manchester in 1900. The foundation of the present industry, however, was laid by the Norwegians, Birkeland and Eyde, in 1902. As at present carried out in Norway, at Notodden and Rjukan, the process utilises 350,000 horse-power, all being derived from water-power.

Air is drawn through a flat circular furnace (Fig. 298), in which an electric arc, burning between water-cooled copper poles, is spread out by an electromagnet into a disc of flame, the temperature of which is about 3000°. In passing through this flame, combination between the oxygen and nitrogen occurs: $N_2 + O_2 \rightleftharpoons 2NO$. At 3000° the equilibrium yield of NO is 5 per cent. by volume; at 1500° it is only 0·4 per cent., since the reaction absorbs heat. The gases leave the furnace at about 1000°, containing 1 per cent. of NO. They pass through iron pipes lined with brick to the firebox of a tubular boiler, where they are cooled to 150°, with production of steam, which is used to evaporate solutions formed in the process. The gas now passes through large aluminium pipes exposed to the air, where it cools to 50°.

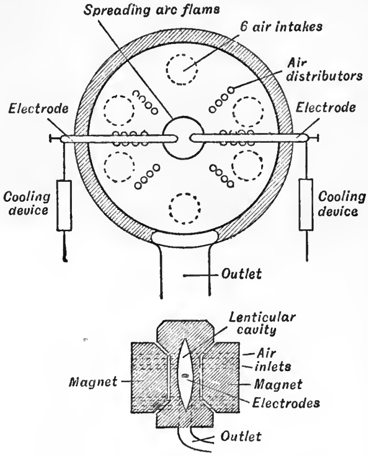


FIG. 298.—Birkeland-Eyde Arc Furnace.

When the gas has cooled below 600°, formation of nitrogen dioxide begins: $2NO + O_2 \rightleftharpoons 2NO_2$; this is a somewhat slow process, and to give time for the reaction to proceed the gases from the air-coolers are passed through a large empty iron oxidising tower. From this the gas passes to the first of three or four gigantic absorption towers, built of granite slabs, 65–80 ft. high and 18 ft. diameter, packed with broken quartz over which water is circulated. In these towers formation of nitric acid occurs, involving the following reactions:

$$2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3.$$
$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O.$$
$$N_2O_3 \rightleftharpoons NO + NO_2.$$

The N_2O_3 is evolved from the solution, then decomposes nearly completely into NO and NO_2. The latter reacts over again, whilst the NO is reoxidised by the excess of air present, forming NO_2, which also enters into reaction. Nearly all the nitrous acid is removed from the solution, and 30 per cent. **nitric acid** runs from the first tower, the acid having been pumped from the final tower through all the towers in succession.

The dilute nitric acid is either neutralised with limestone, to form **calcium nitrate,** which is evaporated and exported as a fertiliser (“ Norge saltpeter ”); or is concentrated by distilling it with concentrated sulphuric acid.

When the gases become very dilute, the oxidation of NO is very slow, so that a mixture of NO and NO_2 passes from the last absorption tower, about 85 per cent. of the oxides of nitrogen having by this time been absorbed. This is passed into an iron tower packed with quartz, down which a solution of sodium carbonate trickles. This absorbs nearly all the residual oxides, with formation chiefly of **sodium nitrite**:

$$NO + NO_2 \rightleftharpoons N_2O_3 \; ; \; N_2O_3 + 2NaOH = 2NaNO_2 + H_2O.$$

The oxidation of ammonia.—In 1795, the Rev. A. Milner, Fellow of Queens' College, Cambridge, found that ammonia, when passed over heated manganese dioxide, is oxidised to red fumes which on dissolving in water form nitric acid. The French chemist Kuhlmann, in 1839, found that ammonia can be oxidised by passing it, mixed with air, over heated platinum: $4NH_3 + 5O_2 = 4NO + 6H_2O$. The colourless gas, on cooling, becomes red from further oxidation of the nitric oxide: $2NO + O_2 = 2NO_2$. It may be absorbed in water, with formation of **nitric acid**, as described under the arc process.

EXPT. 231.—Pass a current of air through ammonia in a wash-bottle, and lead the mixed gas over a small roll of platinum foil heated to dull redness in a hard glass tube. Notice the formation of red fumes in the globe attached to the tube (Fig. 270).

The best results are obtained when the gases are passed very rapidly through the catalyst; with a slow current of gas the NO is broken up again, or reacts with the ammonia: $4NH_3 + 6NO = 5N_2 + 6H_2O$. In the latest type of apparatus (Fig. 299) a mixture of 1 vol. of purified ammonia gas and 7·5 vols. of air, filtered from dust, is passed through two or three pieces of fine platinum gauze stretched across a rectangular aluminium box, and heated electrically. The gases may also be heated to about 500° before passing to the apparatus, and the reaction then proceeds automatically. More than 90 per cent. of the ammonia is oxidised to NO, and the production is very large, since 1 sq. ft. of combined catalyst gauze will effect the production of 1·7 tons of HNO_3 per twenty-four hours. The gases are cooled, and treated in towers as in the arc process.

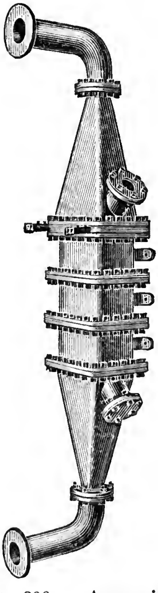


FIG. 299.—Ammonia Oxidation Converter.

If the cooled gas is passed through milk of lime, **calcium nitrate** is produced: the first reaction is

$$2Ca(OH)_2 + 2N_2O_4 = Ca(NO_3)_2 + Ca(NO_2)_2 + 2H_2O.$$

When all the lime is neutralised, nitric acid is formed in the solution by reactions previously explained. This decomposes the nitrite, with evolution of oxides of nitrogen, which are fully oxidised to NO_2 by air and passed into another absorber of milk of lime: $Ca(NO_2)_2 + 2HNO_3 = Ca(NO_3)_2 + NO + NO_2 + H_2O$.

If ammonia gas mixed with air is blown into the cooled and fully oxidised gas from the oxidation apparatus, solid **ammonium nitrate** is deposited as a powder: $4NO_2 + O_2 + 2H_2O + 4NH_3 = 4NH_4NO_3$.

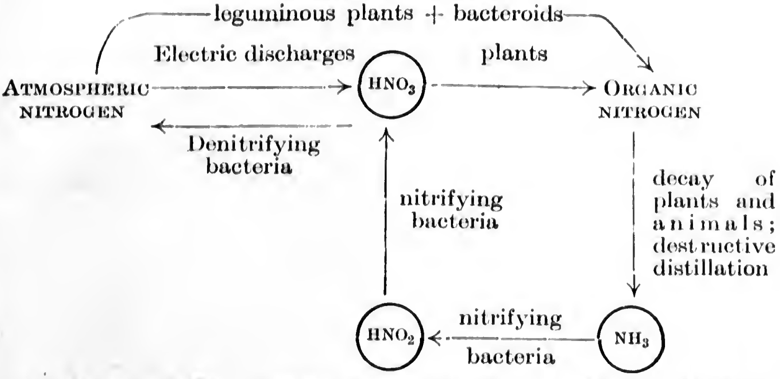
The nitrogen cycle.—Nitric acid is formed by electrical discharges in the atmosphere, and is washed down by rain. It is estimated that no less than 250,000 tons of nitric acid are so produced in twenty-four hours; only a small amount of this falls on fertile soil, and is utilised by plants. Besides the nitric acid produced by electrical discharges, which is absorbed from the soil in the form of nitrates by plants, it is found that leguminous plants can grow and form organic nitrogen compounds (proteins) in air and soil free from ammonia or nitrates. These plants take up atmospheric nitrogen, which is converted into organic nitrogen by the agency of micro-organisms called **bacteroids,** which occur in nodules on the root-hairs. Algæ, fungi, and mosses are also capable of utilising elementary nitrogen. The organic nitrogen compounds elaborated by plants serve as food for herbivorous animals, and the proteins of the latter are utilised in turn by carnivora.

When the bodies of animals and plants decay, or are subjected to destructive distillation, ammonia is produced. In the soil this is oxidised by **nitrifying bacteria** to nitrites, and nitrates, the latter again serving for the nourishment of plants. A portion of the nitrogen, however, is again set free by the action of **denitrifying bacteria.**

The **nitrogen cycle** in Nature may be represented diagrammatically as shown on page 577.

The so-called **nitrogen problem** arises from: (1) the former very large dependence of civilised countries on the single source of supply of nitrates in Chile; (2) the certain exhaustion of these deposits in the near future. All civilised countries have taken steps to render themselves more or less independent of external sources of supply of nitrates: Germany is completely independent in this respect.

NITROGEN CYCLE.



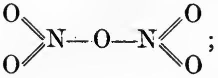
Nitric anhydride, nitrogen pentoxide, N_2O_5.—The anhydride of nitric acid was obtained by Deville (1849) by the action of chlorine on silver nitrate: $4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 + O_2$. It is more conveniently prepared by dehydrating concentrated nitric acid by phosphorus pentoxide (Weber): $2HNO_3 = N_2O_5 + H_2O$.

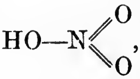
To concentrated pure nitric acid in a stoppered retort, cooled in a freezing mixture, pure phosphorus pentoxide is added in slight excess in small quantities at a time. The mixture is allowed to stand and distilled at a temperature of 30°. The distillate in the cooled receiver consists of two layers: the upper, orange-red, layer solidifies on cooling in a freezing mixture to colourless crystals of N_2O_5. If the distillation is carried out in a current of ozonised oxygen, and the gases are passed through a phosphorus pentoxide tube, perfectly pure crystals of N_2O_5 are obtained by cooling in solid CO_2 and ether.

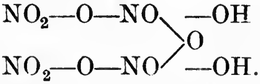
Crystalline nitrogen pentoxide is also formed by passing ozonised oxygen through cooled liquid nitrogen tetroxide: $N_2O_4 + O_3 = N_2O_5 + O_2$.

Nitrogen pentoxide forms white, very hygroscopic crystals, which are stable below 0°, but decompose slowly at the ordinary temperature, even in sealed tubes, becoming yellow: $2N_2O_5 = N_2O_4 + O_2$. The crystals melt with decomposition at 29·5°, and form a dark brown liquid, which decomposes into red fumes of NO_2 and oxygen at 40°. If suddenly heated, the crystals explode; they dissolve with a hissing noise in water, forming nitric acid: $N_2O_5 + H_2O = 2HNO_3$. Phosphorus and potassium burn in the liquid pentoxide if slightly warmed; charcoal does not decompose it even on boiling, but burns brilliantly if previously ignited. Sulphur forms white vapours, condensing to crystals of nitrosulphonic anhydride, $S_2O_5(NO_2)_2$. A crystalline compound, $N_2O_5,2HNO_3$, m.-pt. 5°, is formed on cooling a solution of the anhydride in concentrated nitric acid.

The formula of the anhydride may be written



nitric acid is  , and the compound of the two may be :



In considering the remaining oxides of nitrogen, it will be most convenient to begin with nitric oxide, NO, which is involved in the preparation of some of the other oxides.

Nitric oxide, NO.—Although nitric oxide appears to have been obtained by Mayow, Hales, and Cavendish, it was first recognised as a distinct gas by Priestley (1772), who prepared it by the action of copper or mercury on dilute nitric acid, and called it *nitrous air* : $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$.

EXPT. 232.—Copper turnings are placed in a flask (Fig. 300) and a mixture of equal volumes of concentrated nitric acid and water (sp. gr. 1·2) is poured on. At first, the flask becomes filled with red fumes, due to the action of the nitric oxide on the atmospheric oxygen : $2NO + O_2 = 2NO_2$. When these are driven out, the gas becomes nearly colourless, but always has a slight yellowish tinge, since a little NO_2 is produced by the action of the metal on the acid. This colour is removed when the gas is passed through water, and the jars fill with a colourless gas only slightly soluble in water. The gas so prepared, especially in the later stages of the reaction, contains a variable amount of nitrogen. It may be purified by passing into a cold saturated solution of ferrous sulphate. A nearly black liquid is formed, containing $FeSO_4 \cdot NO$, which on gentle heating evolves nearly pure nitric oxide. The gas so purified still contains 1/500 of its volume not absorbed by fresh ferrous sulphate.

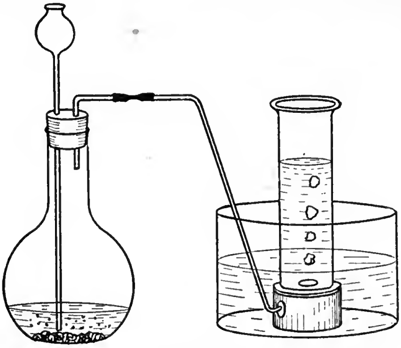


FIG. 300.—Preparation of Nitric Oxide.

Nearly pure nitric oxide may be obtained by heating a mixture of potassium nitrate, ferrous sulphate, and dilute sulphuric acid. A dark brown solution of NO in ferrous sulphate is first formed, which breaks up on heating :

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$$
$$3FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

If a solution of iron in concentrated hydrochloric acid is mixed with an equal volume of the acid, and the solution heated with sodium nitrate, nearly pure nitric oxide is evolved :

$$3FeCl_2 + NaNO_3 + 4HCl = 3FeCl_3 + NaCl + 2H_2O + NO.$$

Perfectly pure nitric oxide is obtained (W. Crum, 1840) by shaking mercury in a flask with concentrated sulphuric acid to which sodium nitrate has been added ; the gas is purified by passing over solid potash. $2HNO_3 + 6Hg + 3H_2SO_4 = 2NO + 3Hg_2SO_4 + 4H_2O$.

This reaction is used in the **estimation of nitrites or nitrates,** or of oxides of nitrogen in commercial sulphuric acid. The substance is dissolved in the least amount of water and passed into the Lunge **nitrometer** (Fig. 301), which consists of a graduated tube, *A*, with a stopcock, *B*, communicating with a small cup, *C*, and an outlet tube, *D*, the whole being filled with mercury and provided with a levelling tube, *E*. Concentrated sulphuric acid is then introduced, and the mixture shaken violently with the mercury. The volume of nitric oxide is read off.

Pure nitric oxide is evolved by dropping a solution of potassium nitrite and potassium ferrocyanide into dilute acetic acid : $K_4FeC_6N_6 + KNO_2 + 2CH_3{\cdot}COOH = K_3FeC_6N_6 + 2CH_3{\cdot}COOK + H_2O + NO$. The gas should be collected over mercury, as it acts slightly on water, evolving traces of nitrous oxide.

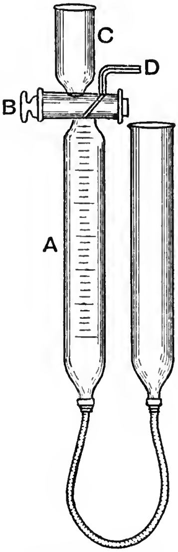


FIG. 301.—Lunge's Nitrometer.

Properties of nitric oxide.—Nitric oxide is a colourless gas, slightly heavier than air (normal density 1·3402 gm./lit.), and sparingly soluble in water :

Temp.	0°	15°	30°	60°
Vols. of NO in 1 vol. of water	0·074	0·051	0·040	0·029

It is difficult to liquefy : the liquid boils at − 153°, and freezes at − 167° to a white solid. The critical temperature is − 93·5°, and the critical pressure 71·2 atm.

Nitric oxide is freely soluble in cold ferrous sulphate solution, forming a black liquid, as was observed by Priestley. The maximum absorption corresponds with $FeSO_4{\cdot}NO$, but the reaction is reversible, the absorption depending on the temperature, the concentration of the ferrous salt (other ferrous salts, *e.g.*, $FeCl_2$, also absorb NO, in different amounts), the pressure, and the presence of other salts : $FeSO_4 + NO \rightleftharpoons FeSO_4{\cdot}NO$. The gas is readily evolved on heating. Manchot regards the compound as $[Fe(NO)]SO_4 \rightleftharpoons FeNO^{\cdot\cdot} + SO_4''$. The cation carries the nitric oxide with it on electrolysis.

Nitric oxide is also absorbed by an acidified solution of potassium permanganate : $6KMnO_4 + 10NO + 9H_2SO_4 = 3K_2SO_4 + 6MnSO_4 + 10HNO_3 + 4H_2O$.

It is not absorbed by alkalies, but dissolves in a mixture of caustic soda and sodium sulphite, forming **sodium nitrosohydroxylamine sulphonate** $Na_2(NO)_2SO_3$ or $ON{\cdot}N(ONa)\,SO_3Na$.

Nitric oxide combines with free oxygen to form red fumes of nitrogen dioxide : $2NO + O_2 = 2NO_2$. The reaction is not complete unless a short time of contact is allowed : this is less than a second with the pure gases, but may amount to several minutes with very dilute mixtures of nitric oxide and air. In contact with water, the red fumes dissolve, forming a mixture of nitrous and nitric acids : $2NO_2 + H_2O = HNO_2 + HNO_3$. If the nitric oxide and oxygen are dried with phosphorus pentoxide they do not combine.

Some combustible substances burn in nitric oxide, but the material must first be ignited in air, and then introduced, freely burning, into the nitric oxide. The latter is the most stable oxide of nitrogen : it begins to decompose into nitrogen and oxygen appreciably only above 1000°, and unless this temperature is attained combustion does not proceed. The substances burn only in the oxygen liberated by the thermal decomposition of the gas. A lighted taper, burning sulphur, and charcoal are extinguished in the gas. Feebly burning phosphorus is also extinguished in the gas, but if burning brightly the combustion continues brilliantly, red fumes being produced as well as white clouds of phosphorus pentoxide : $2NO = N_2 + O_2$; $P_4 + 5O_2 = 2P_2O_5$; $2NO + O_2 = 2NO_2$. A mixture of carbon disulphide vapour and nitric oxide burns with a brilliant blue flame (p. 730).

A mixture of hydrogen and nitric oxide when passed over heated platinum black is reduced to ammonia : $2NO + 5H_2 = 2NH_3 + 2H_2O$. Higher oxides of nitrogen, and nitric acid vapour, are similarly reduced.

Nitric oxide is absorbed by nitric acid ; with concentrated acid a yellow solution of NO_2 is obtained. With more dilute acid a blue (N_2O_3) or green ($NO_2 + N_2O_3$) solution is formed, the blue solution being obtained with the most dilute acid. Beyond a certain dilution the acid absorbs very little of the gas.

The **composition** of nitric oxide may be determined by heating a spiral of iron wire, by an electric current, in a measured volume of gas. The apparatus shown in Fig. 302 may be used. The oxygen is removed by the iron and, after cooling, half the volume of nitrogen is left. The density of the gas is 15 (H = 1), hence the molecular weight is 30. This contains half its volume, or 14 parts, of nitrogen, and 30 — 14 = 16 parts of oxygen, *i.e.*, 1 atom of each element, so that the formula is NO. Nitric oxide does *not* explode with hydrogen unless previously mixed with an equal volume of nitrous oxide.

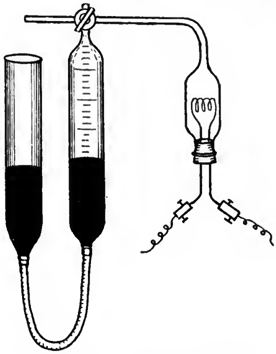


FIG. 302.—Composition of Nitric Oxide.

The analysis of nitric oxide by heating finely-divided nickel in the gas was carefully executed by R. W. Gray (1905). The ratio was :—N : O = 14·0085 : 16. The density of the gas was also found to be 1·3402, so that, after a correction for compressibility, the molecular weight (O=16) = 30·009 ; or N = 30·009 — 16 = 14·009.

The apparatus used in the analysis of NO is shown in Fig. 303. The gas was contained in the bulb *A*, which was weighed, first empty and then full of gas. The platinum boat, *H*, heated by a platinum spiral, contained the nickel. The bulb *M* contained charcoal. After the decomposition was complete, the bulb *M* was put in communication with *A* and immersed in liquid air. The nitrogen condensed on the charcoal, and was weighed. The weight of *A* now gave the weight of oxygen which had combined with the nickel : $2NO + 2Ni = N_2 + 2NiO$.

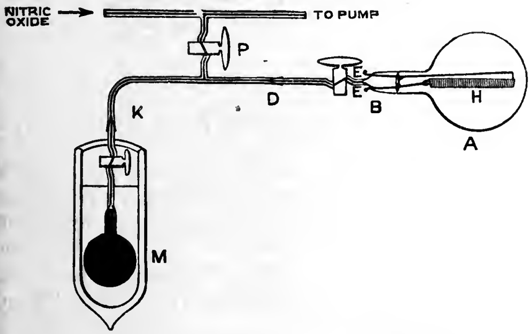


FIG. 303.—Gray's Apparatus for determining the Composition of Nitric Oxide.

Nitrous oxide, N_2O.—Priestley (1772) noticed that if nitrous air (NO) is allowed to stand in contact with moist iron filings, or liver of sulphur, it contracts, like common air, but the residual gas differs completely from that left by common air (N_2) in supporting combustion vigorously. Priestley called the gas *diminished nitrous air*. The gas was carefully examined by Davy in 1799. He first prepared it in the pure state, by heating ammonium nitrate, determined its composition, and examined its physiological action. He called it **nitrous oxide.** Its use as an anæsthetic and its peculiar effects (" laughing gas ") are well known.

Nitrous oxide is produced by the reduction of moist nitric oxide by sulphur dioxide or sulphites, or of nitric acid by metals or stannous chloride under special conditions :

$$4Zn + 10HNO_3 \text{ (dilute)} = 4Zn(NO_3)_2 + 5H_2O + N_2O.$$
$$2HNO_3 + 4SnCl_2 + 8HCl = 4SnCl_4 + 5H_2O + N_2O.$$
$$2NO + SO_2 + H_2O = H_2SO_4 + N_2O.$$

A purer gas is more conveniently obtained by the decomposition of ammonium nitrate by heat (Davy) : $NH_4NO_3 = N_2O + H_2O$. Very pure nitrous oxide is obtained by heating a solution of equimolecular amounts of hydroxylamine hydrochloride and sodium nitrite : $NH_3O + HNO_2 = N_2O + 2H_2O$.

EXPT. 233.—Heat about 50 gm. of pure ammonium nitrate, previously dried at 105°, in a glass retort over wire gauze. The salt melts at 170° (when quite dry ; usually at 165°), and begins to decompose below 200°. The reaction is exothermic : $NH_4NO_3 = N_2O + H_2O +$ 25 kg. cal., and if the salt is heated above 250° it is liable to explode : before this occurs, nitric oxide, nitrogen, and ammonia are evolved.

The gas is purified from higher oxides of nitrogen by passing through potassium permanganate solution, from chlorine (derived from ammonium chloride in the ammonium nitrate) and nitric acid vapour by caustic soda, and from ammonia by concentrated sulphuric acid, and is collected over hot water or mercury.

The nitrate may be mixed with three parts of sand and heated to 260–285° ; a mixture of 2 molecular proportions of $NaNO_3$ with 1 of $(NH_4)_2SO_4$ on heating to 240° evolves a regular stream of nitrous oxide.

Nitrous oxide is prepared for use as a mild anæsthetic ; it is liquefied by compression in steel cylinders. The gas should be carefully purified from chlorine and nitric oxide, as described above.

Properties of nitrous oxide.—Nitrous oxide is a colourless **gas,** normal density 1·9777 gm./lit., with a faint sweetish odour and taste. It is appreciably soluble in water :

Temp.	0°	5°	10°	15°	20°	24°
Vols. of N_2O in 1 vol. of water	1·3052	1·0954	0·9196	0·7778	0·6700	0·5962

The solution has no action on litmus, so that the gas does not behave as the true anhydride of hyponitrous acid : $H_2O + N_2O = H_2N_2O_2$. When cooled to −90°, or exposed to pressure (30 atm. at 0° ; 40 atm. at 15°), it forms a colourless mobile **liquid,** b.-pt. −88·7°; the critical temperature is 35·4°, the critical pressure 75·0 atm. The liquid is lighter than water (sp. gr. 0.908); when cooled to −115°, or when *rapidly* evaporated (not spontaneously on reducing the pressure, as in the case of liquid carbon dioxide), it forms a snow-like mass, with some transparent crystals, of the **solid,** m.-pt. −102·3°.

Nitrous oxide supports combustion more vigorously than air, since it yields on decomposition a gas containing one-third its volume of oxygen, as compared with one-fifth in air: $2N_2O = 2N_2 + O_2$. Nitric oxide gives a gas containing half its volume of oxygen, but does not support combustion so well as air or nitrous oxide. This arises from the circumstance that nitrous oxide is much more easily decomposed by heat than nitric oxide: the latter is stable to about 1000°. Decomposition of nitrous oxide begins at 520°, and is complete at 900°. The gas is also decomposed by sparks, but some nitric oxide is also formed, presumably by recombination of nitrogen and oxygen. All combustions in nitrous oxide are really combustions in the oxygen set free on heating the gas.

EXPT. 234.—A taper burns in the gas with a brilliant flame, and a glowing chip is rekindled as in oxygen. Nitrous oxide, however, is distinguished from oxygen by its smell, its greater solubility in water, and the fact that it does not produce red fumes with nitric oxide.

EXPT. 235.—Brightly burning phosphorus burns in the gas with a brilliant flame, producing clouds of pentoxide, and a little red fume of nitrogen dioxide. (How is the latter formed?) Feebly burning sulphur is extinguished, but if brightly burning, the sulphur continues to burn vigorously with a double flame. The outer, large, flickering, yellow flame corresponds with the reaction $2N_2O = 2N_2 + O_2$, and the inner, bright blue flame to the reaction $S + O_2 = SO_2$. Sodium and potassium burn in the gas to form peroxides, and iron wire burns as in oxygen.

Nitrous oxide is an **endothermic compound,** and is decomposed into its elements by the shock of exploding fulminating mercury. If mixed with detonating gas $(2H_2 + O_2)$, nitrous oxide is also completely decomposed on explosion, and this may be used to determine the **composition** of the gas.

Two vols. of nitrous oxide when mixed with electrolytic gas and exploded leave three volumes of gas (all the electrolytic gas is condensed to liquid water). On treatment with pyrogallol and caustic potash, 1 vol. of oxygen is absorbed, and 2 vols. of nitrogen are left. Davy determined the composition of nitrous and nitric oxides by heating potassium in a measured volume of the gas confined in a bent tube over mercury. After cooling, an equal volume of nitrogen remained. The gas may also be decomposed by a heated spiral of iron wire, as in the case of nitric oxide: in this way Jaquerod and Bogdan (1904) found that 1 vol. of N_2O gave 1·00686 vols. of N_2.

These experiments show that *nitrous oxide contains its own volume of nitrogen.* The relative density of the gas ($H = 1$) is 22, hence the molecular weight is 44. But this contains a molecular weight (*i.e.*, an equal volume) of nitrogen, N_2, of weight 28, and therefore $44 - 28 = 16$ parts, or one atom of oxygen. The formula is therefore N_2O.

The formula may also be established by exploding the gas with hydrogen in a eudiometer. If 20 c.c. of nitrous oxide are mixed with 20 c.c. of hydrogen and exploded, 20 c.c. of nitrogen are left. The hydrogen must have combined with 10 c.c. of oxygen to form liquid water, so that 2 vols. of nitrogen are combined in 2 vols. of nitrous oxide with 1 vol. of oxygen, and the formula is N_2O.

Nitric oxide does not explode with hydrogen, but if mixed with an equal volume of nitrous oxide both gases explode when sparked with hydrogen.

In an experiment a mixture of 20 c.c. of nitrous oxide, 20 c.c. of nitric oxide, and 40 c.c. of hydrogen was exploded. Thirty c.c. of nitrogen remained. Of this, 20 c.c. must be derived from the nitrous oxide:

$$\begin{array}{ccccccc} N_2O & + & H_2 & = & N_2 & + & H_2O\,; \\ 20\text{ c.c.} & & 20\text{ c.c.} & & 20\text{ c.c.} & & \end{array}$$

hence the 20 c.c. of nitric oxide gave $30 - 20 = 10$ c.c. of nitrogen. Again, 20 c.c. of hydrogen are used up by the nitrous oxide, so that $40 - 20 = 20$ c.c. of hydrogen have combined with the oxygen in the 20 c.c. of nitric oxide, which must therefore have been 10 c.c. Thus, 20 c.c. of nitric oxide contain 10 c.c. of nitrogen and 10 c.c. of oxygen; this corresponds with the formula NO:

$$\begin{array}{ccccc} O_2 & + & N_2 & = & 2NO \\ 10\text{ c.c.} & & 10\text{ c.c.} & & 20\text{ c.c.} \end{array}$$

$$\begin{array}{ccccccc} N_2O & + & H_2 & = & N_2 & + & H_2O \\ 20\text{ c.c.} & & 20\text{ c.c.} & & 20\text{ c.c.} & & \\ NO & + & H_2 & = & \frac{1}{2}N_2 & + & H_2O \\ 20\text{ c.c.} & & 20\text{ c.c.} & & 10\text{ c.c.} & & \\ \hline 40\text{ c.c.} & & 40\text{ c.c.} & & 30\text{ c.c.} & & \end{array}$$

Nitrous acid and nitrites.—Scheele (1772) observed that the residue left after heating nitre effervesced with acids and gave red fumes, hence he concluded that it was a salt of a new acid. The residue is **potassium nitrite**: $2KNO_3 = 2KNO_2 + O_2$. The reduction is effected at a lower temperature by fusing potassium or sodium nitrate with lead or copper, lixiviating with water, filtering from the metallic oxide, and evaporating: $NaNO_3 + Pb = NaNO_2 + PbO$. A little caustic soda is formed, which dissolves lead oxide. This is precipitated by a stream of carbon dioxide, or by carefully neutralising the liquid with nitric acid. The crystals of **sodium nitrite** are dried in a centrifugal machine, then in an oven at 50°. They have a yellowish colour, and always contain a certain amount of nitrate. **Potassium nitrite** may be obtained similarly, but does not crystallise well, hence it is precipitated from the solution by alcohol, or fused and cast into sticks.

Purer nitrites are formed by passing the red fumes evolved on heating nitric acid with arsenious oxide (p. 587), and consisting of a mixture of equimolecular amounts of nitric oxide and nitrogen dioxide, $NO + NO_2$, probably in equilibrium with a small quantity of **nitrous anhydride,** N_2O_3, into a solution of caustic potash or soda (sp. gr. 1·38), or their carbonates, out of contact with air : $2KOH + (NO + NO_2) = 2KNO_2 + H_2O$; $Na_2CO_3 + (NO + NO_2) = 2NaNO_2 + CO_2$. Pure potassium nitrite is obtained by decomposing amyl nitrite with alcoholic potash : $C_5H_{11}NO_2 + KOH = C_5H_{11}{\cdot}OH$ (amyl alcohol) $+ KNO_2$.

Both potassium and sodium nitrites are slightly yellow and their concentrated solutions are markedly yellow. The solutions are alkaline, owing to hydrolysis, since nitrous acid is a weak acid : $NO_2' + H_2O \rightleftharpoons HNO_2 + OH'$. **Sodium nitrite** fuses at 213°, and at 15°, 5 parts of $NaNO_2$ dissolve in 6 parts of water. Its crystals are thin flat prisms, moderately deliquescent ; it may be purified by recrystallisation (unlike KNO_2). **Potassium nitrite** occurs in minute short prisms, containing no water but exceedingly deliquescent, and soluble in one-third the weight of water.

Barium nitrite may be obtained as above, using baryta water, but is more conveniently prepared by mixing hot, almost saturated, solutions of sodium nitrite and barium chloride, filtering off the sodium chloride in a hot-water funnel, and allowing the filtrate to crystallise : $2NaNO_2 + BaCl_2 \rightleftharpoons 2NaCl + Ba(NO_2)_2$. The salt is recrystallised, and dried over sulphuric acid, when it forms $Ba(NO_2)_2,H_2O$.

Silver nitrite, $AgNO_2$, is obtained as a white, sparingly soluble precipitate, when an alkali nitrite is added to silver nitrate solution. It is purified by recrystallisation from hot water.

If dilute sulphuric, hydrochloric, or even acetic acid is added to a solution of a nitrite, free **nitrous acid,** HNO_2, is first formed, but is almost completely decomposed with effervescence, red fumes of oxides of nitrogen being liberated. The solution has a pale blue colour, which appears to be due, not to nitrous acid, but to **nitrous anhydride,** N_2O_3 ; this has a deep blue colour in the liquid state.

The blue colour is also communicated to chloroform when shaken with the aqueous solution, although the latter can never be quite decolorised. The decomposition of the nitrous acid in fairly concentrated solutions probably occurs according to the equation: $2HNO_2 \rightleftharpoons N_2O_3 + H_2O \rightleftharpoons NO + NO_2 + H_2O$. In dilute solutions it may decompose according to the equation: $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$, although this may be regarded as the result of the following reactions: (*a*) $4HNO_2 \rightleftharpoons 2NO + 2NO_2 + 2H_2O$; (*b*) $2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3$. The amount of nitrous acid or its anhydride left in aqueous solution never exceeds a few per cent. A pure dilute solution of nitrous acid is obtained by precipitating a solution of barium nitrite with dilute sulphuric acid; it is pale blue in colour, and slowly decomposes, especially on heating, or shaking, with evolution of nitric oxide.

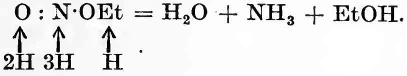
Nitrous acid and nitrites act as **reducing agents**: $HNO_2 + O = HNO_3$; thus they reduce permanganates and chromates. They may be estimated in solution by running into excess of warm acidified standard potassium permanganate (*e.g.*, $N/2$), and titrating the latter with standard oxalic acid: $2KMnO_4 + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$. They are also oxidised by bromine water: $HNO_2 + Br_2 + H_2O = HNO_3 + 2HBr$.

Nitrous acid and nitrites may sometimes act as **oxidising agents**: $2HNO_2 = 2NO + O + H_2O$. In presence of atmospheric oxygen and water, NO will reproduce nitrous acid, so that a small amount of nitrous acid may effect a considerable amount of oxidation by acting as a **carrier of oxygen.** Thus, iodine is liberated from potassium iodide: $2KI + 2HNO_2 = 2KOH + I_2 + 2NO$, indigo is bleached, stannous chloride is oxidised to stannic chloride: $SnCl_2 + 2HCl + 2HNO_2 = SnCl_4 + 2NO + 2H_2O$, sulphur is precipitated from sulphuretted hydrogen, and sulphur dioxide is oxidised to sulphuric acid. The free acid can be titrated with caustic soda and alizarin red.

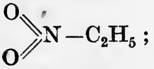
The liberation of iodine from potassium iodide (blue colour with starch) serves as a delicate **test** for nitrous acid (or a nitrite in acid solution). Still more delicate tests are the brown colour with a solution of metaphenylenediamine hydrochloride in hydrochloric acid; and the intense pink colour with a mixture of solutions of sulphanilic acid and α-naphthylamine in acetic acid. These two reactions may be used for the detection and estimation of nitrites in water.

Ammonium nitrite is prepared in solution by the decomposition of barium nitrite by ammonium sulphate. The solution deposits crystals when evaporated in a vacuum at the ordinary temperature. The solid may also be prepared by acting with the red fumes ($NO + NO_2$) from nitric acid and arsenious oxide on lumps of ammonium carbonate (p. 801), extracting the nitrite with absolute alcohol, and precipitating the solution with ether. The crystals are deliquescent, and explode when heated to 70°: $NH_4NO_2 = N_2 + H_2O$.

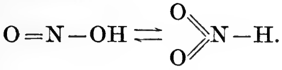
The constitution of nitrous acid.—If ethyl alcohol is distilled with sodium nitrite and sulphuric acid, **ethyl nitrite**, a colourless mobile liquid with a pleasant odour, b.-pt. 17°, is obtained. On boiling with caustic soda this hydrolyses, with the formation of ethyl alcohol and sodium nitrite. The ethyl group appears therefore to be attached to oxygen, not to nitrogen: $O:N{\cdot}O{\cdot}C_2H_5 + NaOH = O:N{\cdot}O{\cdot}Na + C_2H_5{\cdot}OH$. When heated with tin and hydrochloric acid, ethyl nitrite is reduced to ammonia (and hydroxylamine) and alcohol:



$$\underset{\underset{2H}{\uparrow}}{O} : \underset{\underset{3H}{\uparrow}}{N}{\cdot}\underset{\underset{H}{\uparrow}}{O}Et = H_2O + NH_3 + EtOH.$$

If silver or sodium nitrite is heated with ethyl iodide in a sealed tube, **nitroethane**, $C_2H_5NO_2$, isomeric with ethyl nitrite, but boiling at 113–114°, is obtained. This is not hydrolysed by caustic soda, but an atom of hydrogen in the ethyl group, C_2H_5, is replaced by sodium: it therefore behaves as acidic hydrogen, indicating that the ethyl group is attached to a negative group (p. 517), NO_2. On reduction with nascent hydrogen, the ethyl group remains attached to the nitrogen atom, and ethylamine, $C_2H_5{\cdot}NH_2$, which can be obtained by the action of ethyl iodide on ammonia, and therefore has the above formula, is obtained. These reactions indicate that the second compound has the formula ; it is **nitroethane**, *i.e.*, ethane, C_2H_6, with an atom of hydrogen substituted by the nitro-group, NO_2 (p. 569). The reduction may then be formulated: $C_2H_5{\cdot}NO_2 + 6H = C_2H_5{\cdot}NH_2 + 2H_2O$.

Since both compounds may be obtained from sodium nitrite, the latter behaves as a **tautomeric compound**, and there are therefore two tautomeric forms of nitrous acid:



This example shows that evidence of the constitution of inorganic compounds which is based on the reactions of organic compounds must be accepted with caution.

Nitrous anhydride, or nitrogen trioxide, N_2O_3.—Red vapours are obtained by distilling diluted nitric acid with arsenious oxide or starch: $2HNO_3 + As_2O_3 = As_2O_5 + H_2O + N_2O_3$. On cooling the vapours in a freezing mixture, a dark blue volatile liquid is obtained.

EXPT. 236.—Heat 100 gm. of white arsenic with 80 c.c. of nitric acid of sp. gr. 1·35 (56 per cent. HNO_3) in a large flask with a long tube bent slightly backward, as shown, and connected by an ordinary cork with a glass worm cooled with ice and salt (Fig. 304). A deep blue liquid condenses, and is collected in a tube contained in ice and salt.

The tube may be sealed off to preserve the liquid. *Vapours of higher oxides of nitrogen are dangerously poisonous.*

The red gas is absorbed completely by caustic soda, either solid or in solution, with formation of pure nitrites, and by concentrated sulphuric acid, with formation of nitrososulphuric acid. It therefore behaves as if it were **nitrous anhydride,** N_2O_3:

$$2NaOH + N_2O_3 = 2NaNO_2 + H_2O.$$
$$2SO_2(OH)_2 + NO{\cdot}O{\cdot}NO = 2SO_2(OH){\cdot}O{\cdot}NO + H_2O.$$

On the other hand, the vapour density shows that the gas is a mixture of equal volumes of nitric oxide and nitrogen dioxide, so that the compound N_2O_3 is apparently completely dissociated into NO and NO_2. Hasenbach, by passing the vapour from the blue liquid through a red-hot tube, and then through a freezing mixture, obtained a deep blue liquid, the vapour of which, when passed over red-hot copper, gave 36 per cent. of nitrogen, whilst N_2O_3 requires 36·8 per cent. It was therefore considered that nitrous anhydride, although it exists in the liquid state, is completely dissociated as a gas.

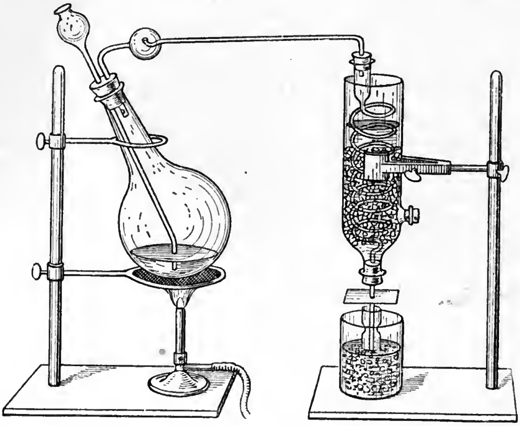


FIG. 304.—Preparation of Nitrogen Trioxide from Arsenious Oxide and Nitric Acid.

Nitrogen dioxide dissociates on heating above 600°: $2NO_2 = 2NO + O_2$. If the hot gas is *rapidly* cooled, oxidation of half the NO occurs rapidly, producing $NO + NO_2$, and as the further oxidation occurs slowly, the gas when passed into a cold tube condenses as N_2O_3.

Ramsay and Cundall (1885) collected gaseous nitrogen dioxide in a tube over mercury, and introduced into it a thin bulb filled with nitric oxide. When the latter was broken there was no change of volume, whereas, according to the experimenters, there should have been a contraction if N_2O_3 is formed :

$$NO + NO_2 = N_2O_3 \text{ (contraction } \tfrac{1}{2}) ; \quad 2NO + N_2O_4 = 2N_2O_3 \text{ (contraction } \tfrac{1}{3}).$$

Dixon and Peterkin (1899) pointed out that if there had been no combination an *expansion* of nearly 10 c.c. should have occurred, due to dissociation of N_2O_4 present in the dioxide owing to its dilution with the other gas: $N_2O_4 \rightleftharpoons 2NO_2$. Since there was really a contraction of about 0·3 c.c., there must have been some reaction leading to diminution of volume, which they assumed to be formation of N_2O_3. With nitrogen dioxide and an indifferent gas, or with NO above 50°, there was the normal expansion of 10 c.c. The gas obtained by mixing 100 vols. of NO and 100 vols. of nitrogen dioxide (NO_2 and N_2O_4) at 27° they calculated should have the following composition:

	N_2O_4.	NO_2.	NO.	N_2O_3.	Total.
Before mixing ...	68	32	100	0	200
After mixing	62	38	94	6	200

If the blue liquid is dried by prolonged exposure to phosphorus pentoxide it may be volatilised without decomposition, and has a vapour density corresponding with N_4O_6; in presence of the least trace of moisture it decomposes: $N_2O_3 \rightleftharpoons NO + NO_2$; a little N_2O_3 still remains in equilibrium, and it is this which causes the reactions described above. As the trace of N_2O_3 is removed by absorbents, it is quickly reproduced, since the equilibrium is disturbed.

Liquid nitrous anhydride is obtained by the action of nitric oxide on solid nitrogen dioxide cooled in liquid air. It is not oxidised to NO_2 by oxygen below −100°, solidifies at −103°, and (unless quite dry) begins to decompose at −21°.

If nitric oxide is mixed with air or oxygen, and the gas *immediately* brought in contact with absorbents, it behaves as N_2O_3 (see above). If it is allowed to stand a few minutes, it behaves as nitrogen dioxide:

(i) $2NO + O_2 = 2NO_2$; (ii) $NO + NO_2 \rightleftharpoons N_2O_3$; (iii) $2NaOH + N_2O_3 = 2NaNO_2 + H_2O$: rapid absorption.

(i) $2NO + O_2 = 2NO_2$ (completely); (ii) $2NO_2 + 2NaOH = NaNO_2 + NaNO_3 + H_2O$: after standing.

These reactions have often been interpreted as if N_2O_3 were the first product of the oxidation of NO by oxygen, and was then further oxidised to NO_2. There is no evidence that this is the case; all the reactions may be explained by the slowing down of the speed of oxidation of NO to NO_2 when half the oxidation has been effected.

EXPT. 237.—To 40 c.c. of NO in a graduated tube over mercury containing 20 c.c. of concentrated potash solution add rapidly 50 c.c. of air. Almost immediate absorption of the red fumes occurs, and 40 c.c. of nitrogen are left ($4NO + O_2 + 4N_2 \rightleftharpoons 2N_2O_3 + 4N_2$). To 20 c.c. of nitric oxide contained in a second tube, without alkali, add 50 c.c. of air. After standing for two minutes add 20 c.c. of potash solution. The red fumes are more slowly absorbed than in the first experiment, and 40 c.c. of nitrogen are left ($2NO + O_2 + 4N_2 = 2NO_2 + 4N_2$). (Gay-Lussac, 1816).

EXPT. 238.—By means of a T-tube admit a *small* amount of NO from a gas-holder into a *rapid* stream of air passing into a flask. When the gas has passed for a few minutes, cork the flask and allow it to stand with a piece of white paper behind. Observe the *slow* appearance of the yellow colour, due to NO_2, indicating the time required for the oxidation of NO in dilute gases (*cf.* p. 574).

Nitrogen dioxide, NO_2, and nitrogen tetroxide, N_2O_4.—If nitric oxide is mixed with oxygen, or a gas containing free oxygen, red fumes are produced. These consist of **nitrogen dioxide**: $2NO + O_2 = 2NO_2$. At temperatures below 140° a portion of the nitrogen dioxide is associated, to form **nitrogen tetroxide**: $2NO_2 \rightleftharpoons N_2O_4$.

If a mixture of 1 vol. of oxygen and 2 vols. of nitric oxide, both gases being dry, is passed *slowly* through a long tube, so as to allow time for complete oxidation, and the gas then passed through a spiral tube cooled in a freezing mixture, a yellow liquid is condensed, which is nitrogen tetroxide. But the reaction $2NO + O_2 = 2NO_2$ requires an appreciable time for its completion, and if the mixed gas is passed *rapidly* into a cooled tube, a green liquid condenses. This is a mixture of nitrogen tetroxide and blue nitrogen trioxide formed from the dioxide and unchanged nitric oxide. If the gases are moist the liquid is always green: $4NO_2 + H_2O = 2HNO_3 + N_2O_3$.

Nitrogen dioxide is produced by the action of *concentrated* nitric acid on copper or bismuth (Priestley): $Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$. It is obtained by the decomposition of lead and copper nitrates by heat: $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$.

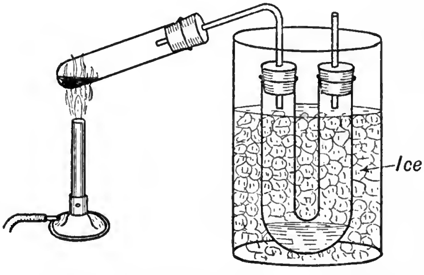


FIG. 305.—Preparation of Nitrogen Dioxide by Heating Lead Nitrate.

EXPT. 239.—Heat dry powdered lead nitrate in a hard glass tube or retort, and pass the red gas through a U-tube cooled in a mixture of ice and salt (Fig. 305). A yellow liquid collects in the cooled tube. Hold a glowing chip over the exit of the U-tube: it bursts into flame, showing that oxygen is also evolved. Pour the N_2O_4 on crushed ice in a test-tube. A deep blue layer of N_2O_3 separates: $N_2O_4 + H_2O \rightleftharpoons HNO_2 + HNO_3$; $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$. On warming, red fumes are evolved (Fritzsche).

This is a very unsatisfactory method of preparing nitrogen dioxide in quantity. It is more conveniently prepared by the action of nitric acid and phosphorus pentoxide on a mixture of nitrous anhydride and nitrogen dioxide obtained by distilling arsenious oxide with a mixture of concentrated nitric acid and half its weight of concentrated sulphuric acid (Cundall, 1891): $N_2O_3 + 2HNO_3 \rightleftharpoons 2N_2O_4 + H_2O$.

Expt. 240.—To the blue liquid obtained by distilling As_2O_3 with nitric acid, and condensing in a freezing mixture, add excess of P_2O_5, and fuming nitric acid drop by drop until the colour changes to yellow. The mixture should be kept well cooled during the reaction. Distil off through a worm cooled in ice, rejecting the first few c.c., which are coloured green. Collect in a tube immersed in ice, and seal off.

The most convenient method is to heat nitrososulphuric acid with sodium nitrate:

$$SO_2(OH){\cdot}O{\cdot}NO + NaNO_3 = N_2O_4 + NaHSO_4.$$

Expt. 241.—Pass sulphur dioxide into cooled fuming nitric acid until the liquid becomes a pasty mass of crystals of nitrososulphuric acid. Add dry sodium nitrate. Warm, and collect the N_2O_4 as above.

Properties of nitrogen dioxide.—Nitrogen di- (or tetr-) oxide in a good freezing mixture solidifies to pale yellow, nearly colourless crystals, melting at −10·95° to a honey-yellow liquid. The solid probably consists almost entirely of N_2O_4, which appears to be colourless. The liquid at the melting point already contains a trace of NO_2, which is strongly coloured. On warming, the colour of the liquid deepens; at 10° it is distinctly yellow, at 15° it is orange, and the colour darkens until at 21·6° it is reddish-brown, and then the liquid boils, giving a reddish-brown vapour. The colour of the vapour also darkens on further heating, as may be seen by comparing two globes containing it, one maintained at the ordinary temperature: at 40° the vapour has a very deep, almost black, colour.

The colour change on heating is accompanied by a decrease in vapour density up to 140°, when the density becomes constant, and corresponds with NO_2: the intermediate densities correspond with the **dissociation**: $N_2O_4 \rightleftharpoons 2NO_2$, and the percentage dissociation, or the percentage of NO_2 molecules in the vapour, may be calculated by the formula given on p. 153.

Temperature	Vapour density. Δ (H = 1)	Percentage NO_2 in vapour, by volume
26·7°	38·3	20·00
60·2	30·1	52·04
100·1	24·3	89·23
135·0	23·1	98·69
140·0	22·96	100·00

If the vapour is heated above 140°, the density further decreases, but the colour becomes paler, until at 620° the gas is again colourless. This corresponds with the dissociation: $2NO_2 \rightleftharpoons 2NO + O_2$, which is complete at 620°. Recombination occurs on cooling, the series of changes being passed through in the reverse order:

$$N_2O_4 \text{ solid} \underset{-11^\circ}{\rightleftharpoons} N_2O_4 \text{ liq.} \underset{26^\circ}{\rightleftharpoons} N_2O_4 \text{ (vap.)} \underset{140^\circ}{\rightleftharpoons} 2NO_2 \underset{620^\circ}{\rightleftharpoons} 2NO + O_2.$$

At 60·2° the vapour density is 30·1. The (theoretical) vapour density of N_2O_4 is 46, that of NO_2 is 23

$$\therefore \text{ degree of dissociation } \gamma = \frac{46 - \Delta}{23} = \frac{46 - 30{\cdot}1}{23} = 0{\cdot}691.$$

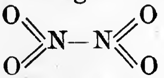
This is the fraction *by volume* of the vapour consisting of NO_2. The fraction of N_2O_4 is 1·000 − 0·691 = 0·309, and since this corresponds with 2 × 0·309 = 0·618 vol. of NO_2, the fraction of NO_2 *by weight* is $\frac{0{\cdot}691}{0{\cdot}691 + 0{\cdot}618} = 0{\cdot}520$.

The action of water on nitrogen dioxide has already been described (p. 574). The composition of the gas is ascertained by passing it over red-hot copper: $4Cu + 2NO_2 = 4CuO + N_2$.

Nitrogen dioxide vapour does not support the combustion of a taper, but strongly burning phosphorus and carbon burn in it. The gas is probably decomposed by the temperature of the flame into nitrogen and oxygen, or nitric oxide and oxygen. Potassium inflames spontaneously in the gas; heated sodium burns in it; and a spiral of iron wire heated to 500° also combines with the oxygen, leaving half the volume of nitrogen: $2NO_2 = N_2 + 2O_2$. The composition of the gas may be determined in this way. Tin is oxidised to the dioxide, carbon monoxide to the dioxide at the ordinary temperature; hydrogen sulphide deposits sulphur, and the nitrogen dioxide is reduced to nitric oxide: $NO_2 + H_2S = NO + H_2O + S$. A mixture of the gas and hydrogen is reduced to ammonia on passing over platinum sponge.

Nitrogen dioxide is absorbed by concentrated sulphuric acid with formation of nitrososulphuric acid and nitric acid: since these substances decompose each other, a state of equilibrium is attained: $N_2O_4 + H_2SO_4 \rightleftharpoons SO_2(OH){\cdot}O{\cdot}NO + HNO_3$. The gas is absorbed by alkalies with formation of a mixture of nitrite and nitrate: $2KOH + N_2O_4 = KNO_2 + KNO_3 + H_2O$. Baryta becomes incandescent at 200° in the gas: $2BaO + 2N_2O_4 = Ba(NO_2)_2 + Ba(NO_3)_2$. Quicklime, and oxides of zinc, aluminium, and lead, absorb the gas on heating, but free nitrogen, to the extent of 30 per cent. of the NO_2, is liberated: $4CaO + 5N_2O_4 = 4Ca(NO_3)_2 + N_2$. Nitrites are also formed.

By passing nitrogen dioxide over finely-divided reduced copper, nickel, or iron in the cold, Sabatier and Senderens (1893) obtained compounds called **nitroxyls.** **Copper nitroxyl** is a brown substance, of the formula $Cu(NO_2)_2$, decomposed at 90°: $Cu(NO_2)_2 \rightleftharpoons Cu + 2NO_2$, and by water, with formation of nitrate, copper, and nitric oxide.

The formula of nitrogen dioxide is probably $O{=}\overset{IV}{N}{=}O$; that of the tetroxide , although Divers regards it as a true **peroxide**: O:N·O·O·N:O, and O:N·O.

Pernitric acid.—Hautefeuille and Chappuis, and Berthelot (1881), claimed to have obtained a higher oxide, N_2O_6 or N_2O_7, by the action of a silent discharge or a mixture of nitrogen and oxygen: with water it was supposed to form **pernitric acid**, HNO_4. The existence of these substances is highly doubtful.

Hyponitrous acid, $H_2N_2O_2$.—Divers (1871), by reducing a solution of sodium nitrite or nitrate with sodium amalgam, obtained a liquid which, after neutralisation with acetic acid, gave a *yellow* precipitate with silver nitrate. This had the empirical formula AgNO, and was regarded by its discoverer as the salt of **hyponitrous acid.** Subsequent investigations showed that the acid really had the doubled formula $H_2N_2O_2$.

Sodium hyponitrite, $Na_2N_2O_2$, is easily prepared by Divers' process. Excess of sodium amalgam is added to a solution of sodium nitrite: the reaction evolves heat, and by the prolonged action of the amalgam any hydroxylamine formed is removed. The resulting ammonia is removed by exposing the solution to concentrated sulphuric acid in a vacuum desiccator. Granular crystals of sodium hyponitrite, $Na_2N_2O_2,5H_2O$, slowly separate. They are washed with alcohol, and again exposed in the vacuum desiccator, when they fall to a white powder of anhydrous salt, $Na_2N_2O_2$, stable in air.

The nitrite is supposed to be reduced to the sodium compound of **dihydroxylamine,** $NH(OH)_2$, which is decomposed by the alkali:

$$2Na + 2H_2O + NaNO_2 = NaN(OH)_2 + 2NaOH$$
$$2NaN(OH)_2 = Na_2N_2O_2 + 2H_2O.$$

Hyponitrous acid is also formed in small quantities by the action of nitrous acid on hydroxylamine:

$$HO - N\boxed{H_2 + O} : N{\cdot}OH = HO{\cdot}N{:}N{\cdot}OH + H_2O.$$

EXPT. 242.—To a solution of hydroxylamine hydrochloride add sodium nitrite and acetic acid. Heat rapidly to 60°, then add silver nitrate solution. A yellow precipitate of silver hyponitrite is formed.

Sodium hyponitrite is most conveniently prepared by boiling sodium hydroxylamine sulphonate (p. 553) with caustic soda: $2HO{\cdot}NH{\cdot}SO_3Na + 4NaOH = Na_2N_2O_2 + 2Na_2SO_3 + 4H_2O$.

If silver hyponitrite is added gradually to an ethereal solution of hydrogen chloride in absence of moisture, and the filtered solution evaporated *in vacuo*, crystalline explosive laminæ of free **hyponitrous acid**, $H_2N_2O_2$, are formed. The solution decomposes on heating with evolution of nitrous oxide: $H_2N_2O_2 = H_2O + N_2O$.

EXPT. 243.—Warm a little sodium hyponitrite with dilute sulphuric acid. Nitrous oxide is evolved with effervescence, and kindles a glowing chip.

Hyponitrites in acid solution reduce permanganate: $5H_2N_2O_2 + 8KMnO_4 + 12H_2SO_4 = 10HNO_3 + 4K_2SO_4 + 8MnSO_4 + 12H_2O$. In alkaline solution a nitrite is formed.

The doubled formula of the acid is supported by the following evidence:

1. **Acid** and **normal salts** are known: KHN_2O_2 and $K_2N_2O_2$. The neutral point on titration is reached with KHN_2O_2.
2. The freezing point of the solution of the acid corresponds with $H_2N_2O_2$.
3. By the action of ethyl iodide on silver hyponitrite, **ethyl hyponitrite** is obtained, the vapour density of which corresponds with the formula $(C_2H_5)_2N_2O_2$.
4. By oxidising hydroxylamine with silver oxide, hyponitrous acid, an intermediate acid, **nitrohydroxylamic acid**, $H_2N_2O_3$, and finally nitrous acid, are obtained:

$$2NH_2{\cdot}OH \rightarrow H_2N_2O_2 \rightarrow H_2N_2O_3 \rightarrow H_2N_2O_4(2HNO_2).$$

Nitrohydroxylamic acid.—If methyl nitrate is added to a solution of free hydroxylamine and caustic soda in methyl alcohol, the sodium salt of **nitrohydroxylamic acid,** $Na_2N_2O_3$, is obtained. This is very readily oxidised by the air, with formation of nitrite and nitrate, and is decomposed by boiling with water: $2Na_2N_2O_3 + H_2O = 2NaNO_2 + N_2O + 2NaOH$. When the solid salt is gently heated, it decomposes into nitrite and hyponitrite. On acidifying, the free acid liberated at once decomposes into nitric oxide and water: $H_2N_2O_3 = 2NO + H_2O$. The constitution of the acid appears to be $HO{\cdot}N{:}NO_2H$.

Nitrosyl chloride, NOCl.—The chloride of nitrous acid, **nitrosyl chloride,** NOCl, is formed when nitric and hydrochloric acids are mixed: $HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$. A mixture of 1 vol. of concentrated nitric acid and 3 vols. of concentrated hydrochloric acid was called by the alchemists *aqua regia* because it is capable of dissolving gold (" the king of metals "). It owes this action to the presence of free chlorine. On warming *aqua regia*, an orange-yellow gas is evolved, which is a mixture of chlorine and nitrosyl chloride (Gay-Lussac, 1848). If the gas is dried by calcium chloride and passed through concentrated sulphuric acid, the chlorine passes on, whilst the nitrosyl chloride is absorbed as nitrososulphuric acid: $NOCl + SO_2(OH)_2 = SO_2(OH)\cdot O\cdot NO + HCl$. If the liquid is dropped on sodium chloride, and warmed, pure nitrosyl chloride is evolved: $SO_2(OH)\cdot O\cdot NO + NaCl = SO_2(OH)ONa + NOCl$.

Nitrosyl chloride is also formed by the direct combination of nitric oxide and chlorine in bright sunlight, or in presence of animal charcoal at 40–50°: $2NO + Cl_2 = 2NOCl$. Since it is the acid chloride of nitrous acid, it is also formed by the action of phosphorus pentachloride on potassium nitrite: $PCl_5 + KNO_2 = NOCl + POCl_3 + KCl$.

Nitrosyl chloride is an orange-yellow gas with a suffocating odour, easily condensed in a freezing mixture to a ruby-red liquid, b.-pt. 5·6°, freezing in liquid air to a lemon-yellow solid, m.-pt. $-$ 60°. It is readily decomposed by water and alkalies, in the normal manner: $NOCl + 2KOH = KNO_2 + KCl + H_2O$. It has no action on gold or platinum, but attacks mercury: $Hg + NOCl = HgCl + NO$, and most other metals. It is stable up to 700°, but then dissociates: $2NOCl \rightleftharpoons 2NO + Cl_2$. It forms compounds with many metallic chlorides, *e.g.*, $ZnCl_2,NOCl$; $FeCl_3,NOCl$, and is used in organic chemistry, since it readily adds on to ethylene linkages:

$$>C=C< + NOCl \rightarrow >C(NO)\cdot ClC<.$$

Nitrosyl bromide, NOBr, a blackish-brown liquid, b.-pt. $-$ 2°, is formed by passing nitric oxide into bromine at $-$ 15°. At the ordinary temperature $NOBr,Br_2$ is formed. **Nitrosyl fluoride,** NOF, is a gas, b.-pt. $-$ 56°, m.-pt. $-$ 134°, formed by the reaction $NOCl + AgF = NOF + AgCl$. **Nitrosyl perchlorate,** $NOClO_4$, is formed by passing $NO + NO_2$ into very concentrated perchloric acid.

The chloride of nitric acid, NO_2Cl, is unknown, but **nitryl fluoride,** NO_2F, is formed by the reaction $4NO + F_2 = 2NO_2F + N_2$, at the temperature of liquid oxygen. It is a gas, b.-pt. $-$ 63·5°, m.-pt. $-$ 139°.

Nitrosyl sulphate, nitrososulphuric acid, or "chamber crystals," NO·HSO$_4$.—This important compound, which is supposed to be formed as an intermediate stage in the lead chamber process (p. 505), can be obtained in a number of ways.

It was obtained by Clement and Desormes by the interaction of red fumes of oxides of nitrogen, sulphur dioxide, and a regulated amount of moisture:

$$NO + NO_2 + SO_2 + H_2O = 2SO_2(OH)\cdot O\cdot NO.$$

It is more conveniently prepared by passing the red vapours from arsenic trioxide and nitric acid (p. 587) into concentrated sulphuric acid: the acid soon deposits crystals of the compound: $\boxed{NO + NO_2 \rightleftharpoons} \; N_2O_3 + H_2SO_4 \rightleftharpoons SO_2(OH)\cdot O\cdot NO + H_2O$. These decompose with effervescence, evolving red fumes, when treated with water, so that the reaction is reversible. They dissolve in concentrated sulphuric acid, and in sulphuric acid containing not more than 35 per cent. of water, but if the acid is diluted below 65 per cent. H_2SO_4, decomposition occurs, and the nitrogen compounds are then almost completely expelled.

Expt. 244.—Pass red fumes from arsenious oxide and nitric acid (p. 587) into cooled concentrated sulphuric acid. Observe the formation of colourless crystals of nitrososulphuric acid. Pour off the liquid acid and dilute with 40 per cent. sulphuric acid. Observe the colour change: yellow, green, blue, and the sudden effervescence at a certain dilution.

Nitrososulphuric acid may also be prepared by passing sulphur dioxide into cooled fuming nitric acid:

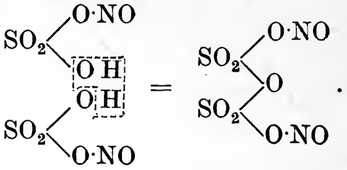
$$2SO_2 + 2HNO_3 = 2SO_2(OH)\cdot O\cdot NO.$$

The crystals are drained on a porous tile.

Nitrosyl sulphate, $NO\cdot HSO_4$, is **nitrososulphuric acid,**

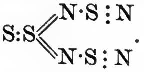
$$NO\cdot O\cdot SO_2(OH).$$

It is sometimes called **nitrosulphonic acid,** and its formula written $NO_2\cdot SO_2\cdot OH$. The crystals melt with decomposition at 73°; water is split off, and **dinitropyrosulphuric acid,** $S_2O_5(O\cdot NO)_2$, formed:



This is a white crystalline substance, m.-pt. 217°, b.-pt. 360°, also obtained by passing nitrogen dioxide into liquid sulphur dioxide: $2SO_2 + 3NO_2 = (NO)_2S_2O_7 + NO$, or by heating the white solid, **oxynitrososulphuric anhydride,** $(NO_2\cdot SO_3)_2$, obtained by the direct combination of nitrogen dioxide and sulphur trioxide: $(NO_2\cdot SO_3)_2 = (NO)_2S_2O_7 + O$.

Nitrososulphuryl chloride, $Cl\cdot SO_2\cdot O\cdot NO$, is a crystalline solid, formed by the direct combination of sulphur trioxide and nitrosyl chloride, or by the action of thionyl chloride on silver nitrate.

Nitrogen sulphides.—Nitrogen sulphide, N_4S_4, is an orange-red crystalline solid, obtained by the action of dry ammonia on a solution of sulphur chloride and chlorine, or on thionyl chloride. It decomposes at 185°, is explosive on percussion, and is decomposed by cold water. It combines with chlorine to form a tetrachloride, $N_4S_4Cl_4$, and reacts with S_2Cl_2 to form **thiazyl chloride,** N_3S_4Cl, which is converted by nitric acid into a crystalline nitrate, $N_3S_4\cdot NO_3$. The molecular weight of nitrogen sulphide in solution corresponds with the formula N_4S_4; it is supposed to have the constitution  $\mathrm{S{:}S}\begin{array}{l}\diagup \mathrm{N\cdot S:N}\\ \diagdown \mathrm{N\cdot S:N}\end{array}$. **Nitrogen pentasulphide,** N_2S_5, is formed, as a deep red liquid, when N_4S_4 is treated with carbon disulphide at 100°. It decomposes on heating.

Sulphonic acids of ammonia and hydroxylamine.—Some products of the action of nitrites on sulphites have already been described (p. 553). The first product appears to be **hydroxylamine disulphonic acid**:

$$HO{\cdot}NO + 2H{\cdot}SO_3H = HO{\cdot}N(SO_3H)_2 + H_2O.$$

This may undergo hydrolysis or further sulphonation:

$HO{\cdot}N(SO_3H)_2 + H_2O = HO{\cdot}NH{\cdot}SO_3H$ (**hydroxylamine sulphonic acid**) $+ H_2SO_4$.

$HO{\cdot}N(SO_3H)_2 + H{\cdot}SO_3H = N(SO_3H)_3$ (**nitrilosulphonic acid**) $+ H_2O$.

These substances are intermediate products in the oxidation of sulphurous to sulphuric acid by means of nitrous acid.

$N(SO_3H)_3$ is a derivative of ammonia; by boiling its salts for a short time with water, they form salts of **imidodisulphonic acid,** $NH(SO_3H)_2$: $N(SO_3K)_3 + H_2O = NH(SO_3H)_2 + KHSO_4$. On further hydrolysis, salts of **amidosulphonic acid,** $NH_2{\cdot}SO_3H$, are formed. **Sulphamide,** $SO_2(NH_2)_2$, and **sulphimide,** $(SO_2NH)_3$, derived from sulphuric acid, $SO_2(OH)_2$, are formed by the action of ammonia on a solution of sulphuryl chloride, SO_2Cl_2, in benzene. Many other compounds of the above types are known.

EXERCISES ON CHAPTER XXIX

1. What oxides of nitrogen may be obtained by the action of nitric acid on metals? How are the reactions explained?
2. How is nitric acid manufactured from the atmosphere? Describe the reactions which take place in each stage of the process.
3. How is nitric acid obtained from (*a*) saltpetre, (*b*) ammonia? How may it be reconverted into ammonia?
4. Describe the preparation of the following compounds in a state of purity: (*a*) nitric oxide, (*b*) nitrous oxide, (*c*) nitrogen dioxide, (*d*) nitrosyl chloride. What are their properties?
5. How is nitrous anhydride prepared? What is the action of the substance on (*a*) water, (*b*) caustic soda, (*c*) concentrated sulphuric acid?
6. How may the composition of (*a*) nitrous oxide, (*b*) nitric oxide, (*c*) nitrogen dioxide, be found?
7. Give examples of the oxidising and reducing reactions of nitrous acid. What evidence is there as to the structural formula of this substance?
8. How is hyponitrous acid obtained? What is its structural formula?
9. How is nitrososulphuric acid prepared? What is the action of (*a*) water, (*b*) nitric acid, on this substance?

CHAPTER XXX

THE INACTIVE ELEMENTS

The ratio of specific heats of a gas.—If 1 gm. mol. of a gas is heated at constant volume from T° to $(T+1)^\circ$ abs., the heat absorbed is called the **molecular heat at constant volume**, $C_v = Mc_v$, where M = molecular weight, c_v = **specific heat at constant volume.** When a gas is heated at a constant pressure of 1 atm. it expands, doing work against the atmospheric pressure, and the heat absorbed is called the **molecular heat at constant pressure,** $C_p = Mc_p$.

If the gas is ideal, *i.e.*, obeys the law : $pv = RT$, no heat absorption results from the change of *volume* alone (*cf.* p. 258), and the **difference of molecular heats**, $(C_p - C_v)$, will be equal to the **external work** done, viz. (*pressure*) × (*increase of volume*) :

$$\therefore C_p - C_v = p\,(V' - V) = pV\left(\frac{T+1}{T} - 1\right) = \frac{pV}{T}$$

$$= R = 1\cdot98 \text{ gm. cal.}$$

In a **monatomic gas** the heat absorbed goes exclusively to increase the **kinetic energy of translation** of the molecules (p. 262), and for 1° rise of temperature this increase of energy will be $\frac{1}{273}\left(\frac{MG^2}{2}\right)$.

But $pv = \frac{1}{3}MG^2 \quad \therefore \frac{1}{273}\left(\frac{MG^2}{2}\right) = \frac{pv}{273}\cdot\frac{3}{2} = \frac{3}{2}R = 2\cdot97$ gm. cal. Hence, for a monatomic gas, **$C_v = 2\cdot97$ gm. cal.** But $C_p = C_v + R = 4\cdot95$ gm. cal., hence the **ratio of specific heats,** C_p/C_v, or c_p/c_v, usually denoted by γ, is equal to $\frac{4\cdot95}{2\cdot97} = 1\cdot667$ for a monatomic gas.

If the gas molecule contains more than one atom, part of the heat supplied at constant volume is used up in increasing the **kinetic energy of rotation** of the molecule, considered as a rigid body ; in addition, the **energy of vibration** of the atoms may be increased if the molecule is not a rigid structure. If this extra energy is denoted by E, per 1° rise of temperature, we shall have :

$$C_p/C_v = \frac{\frac{3}{2}R + R + E}{\frac{3}{2}R + \quad R},$$

which is *less* than 1·667. It is found that C_p/C_v, for polyatomic gases, is always less than 1·667, and is all the lower the more atoms there are in the molecule :

GAS.	FOR-MULA.	RATIO C_p/C_v.	GAS.	FOR-MULA.	RATIO C_p/C_v.
Helium	He	1·667	Carbon dioxide	CO_2	1·308 (0°)
Oxygen	O_2	1·398	Nitrous oxide	N_2O	1·324 ,,
Nitrogen	N_2	1·402	Ammonia	NH_3	1·325 ,,
Air	$4N_2 + O_2$	1·403	Sulphur dioxide	SO_2	1·232 (20°)
Hydrogen	H_2	1·408	Hydrogen sulphide	H_2S	1·343 ,,
Carbon monoxide	CO	1·402	Methane	CH_4	1·313
Hydrogen chloride	HCl	1·401	Ethylene	C_2H_4	1·255 (0°)
Chlorine	Cl_2	1·353	Steam	H_2O	1·33 (100°)

Even in the case of gases containing the same number of atoms in the molecule (O_2, Cl_2 ; CO_2, N_2O ; SO_2, H_2S), the ratio γ has different values ; the lower values probably indicate the presence of additional rotations or vibrations in the molecules to which they refer.

The value of $C_p/C_v = \gamma$ for a gas may be determined in two ways : (1) By allowing the gas, compressed to pressure p_1 in a large globe, to expand suddenly (**adiabatic expansion**) to atmospheric pressure, p_2, by opening a valve, and measuring the temperatures T_1 and T_2, before and after the expansion, respectively, by means of a loop of fine platinum wire (0·001 mm. diam.) placed in the centre of the globe, and used as a resistance thermometer ; $p_1/p_2 = (T_1/T_2)^{\frac{\gamma}{\gamma-1}}$. (2) From the **velocity of sound** in the gas : $u = \sqrt{\gamma\frac{p}{D}}$ where p = pressure, D = density. But $p = \frac{RT}{v}$, and $D = M/v$, $\therefore\ p/D = RT/M$, $\therefore\ u = \sqrt{\gamma\frac{RT}{M}}$. If p is in dynes per cm.², D in gm. per c.c., u will be in cm. per sec. In corresponding units, $R = 8{\cdot}25 \times 10^7$.

A convenient method is to set up stationary waves in the gas, contained in a thoroughly dry sealed tube clamped in the middle, and brought into resonance by affixing discs of lead to the ends by sealing wax (Fig. 306). The gas is caused to vibrate by stroking the tube with a wet cloth, and the positions of the nodes and loops is indicated by lycopodium powder, or silica dust, inside the tube. One end of the tube is placed at the end of an open tube, also containing dust, the air in which is caused to vibrate in resonance with the gas tube. The half wave-length, $\lambda/2$, is the distance from node to node, or loop to loop, which is measured directly. If n is the frequency, $u = n\lambda$, hence for

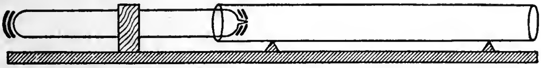


FIG. 306.—Behn and Geiger's Method for Determining the Ratio of Specific Heats of a Gas.

the gas and air, respectively, $u_1/u_2 = n\lambda_1/n\lambda_2$; $\therefore \lambda_1^2/\lambda_2^2 = \gamma_1 M_1/\gamma_2 M_2$. For air, $\gamma_2 = 1{\cdot}403$, and $M_2 = 29$, hence γ_1 may be calculated.

The value $\gamma = 1{\cdot}667$ was found for mercury vapour by Kundt and Warburg (1876), thus confirming the monatomic character of the mercury molecule (p. 146).

This conclusion is necessary if the kinetic theory is accepted. The assumption that the molecules of the inactive gases (argon, etc.), which give the same ratio, are polyatomic, but that the atoms are "bound by such enormous forces that they cannot be separated by chemical affinity," therefore involves a denial of the kinetic theory—a contingency which it must be assumed had not been realised. Any molecular structure, *no matter how rigid,* which is not perfectly symmetrical (*i.e.*, monatomic) must possess *rotational* energy, and the maximum value of C_p/C_v for such a molecule is 1·400.

THE INACTIVE GASES.

Argon.—In 1785, Cavendish, in his attempts to prove that the nitrogen of the atmosphere is all of one kind, noticed that a small residue was left on sparking with oxygen over caustic potash (p. 566). Until 1894 it was taken for granted that atmospheric nitrogen was homogeneous, but in that year Lord Rayleigh, in his accurate determinations of the densities of gases (p. 71), noticed that nitrogen prepared from the atmosphere is slightly heavier than that prepared from oxides of nitrogen reduced by heated iron, from ammonium nitrite, or from urea and sodium hypobromite: Normal density: (*a*) "chemical" nitrogen = 1·25107; (*b*) atmospheric nitrogen = 1·25718.

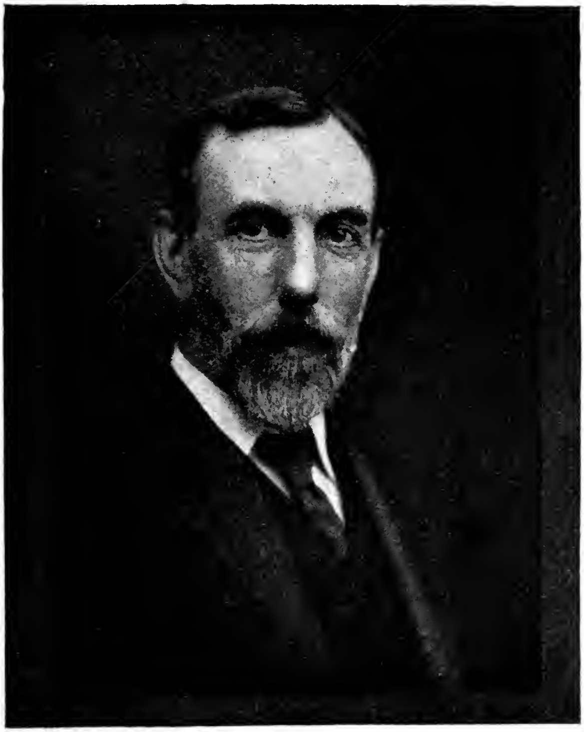
This difference did not escape such an accurate observer, and a repetition of Cavendish's experiment confirmed the presence of a small unabsorbed residue, which did not give the spectrum of nitrogen.

In conjunction with Sir William Ramsay, Rayleigh now attempted to prepare the new gas from atmospheric nitrogen in quantities sufficient to permit of a careful examination of its properties. Two methods were employed: (i) absorption of the nitrogen by red-hot magnesium; (ii) conversion of the nitrogen into nitric acid by sparking with oxygen in presence of an alkali.

1. The oxygen of air was absorbed by passing over red-hot copper, and the residual nitrogen then repeatedly passed over heated magnesium. The nitrogen was slowly absorbed as magnesium nitride, Mg_3N_2, and the unabsorbed residue was collected and examined. The apparatus used is shown in Fig. 307. The atmospheric nitrogen, contained in a gas-holder, *A*, was passed through drying tubes and then through a tube, *G*, containing red-hot magnesium. The gas was collected in the gas-

holder, *B*. It was then passed back again, and the process repeated until no further absorption took place; the volume of the gas was reduced to 1/80th. Further treatment raised the density of the gas to 19·94 (H = 1).

2. A mixture of 11 vols. of oxygen and 9 vols. of air was passed (Fig. 308) into a 50-litre glass globe, provided with heavy platinum electrodes. A discharge from a transformer of 6000–8000 volts was passed between the electrodes, and a fountain of caustic soda solution discharged over the inside of the globe. With a consumption of energy of 1 horse-power, 20 litres of gas were absorbed per hour. The oxygen was absorbed from the residual gas by pyrogallol and alkali.



Sir William Ramsay.

The new gas was distinguished from all other elements by its entire inertness. It is not absorbed by heated metals, copper oxide, caustic potash, potassium permanganate, sodium peroxide, phosphorus, etc., nor does it react when sparked with oxygen, hydrogen, chlorine, or even fluorine. It is unchanged when an arc is maintained in the gaseous or liquid substance for several hours. On this account, Ramsay called the gas **argon** (Greek *argon*, lazy, or inactive). Berthelot, however, in 1895, stated that a contraction occurred when a mixture of argon and benzene vapour was subjected to the silent discharge: this is the sole experiment indicating any activity of argon, and it is unconfirmed.

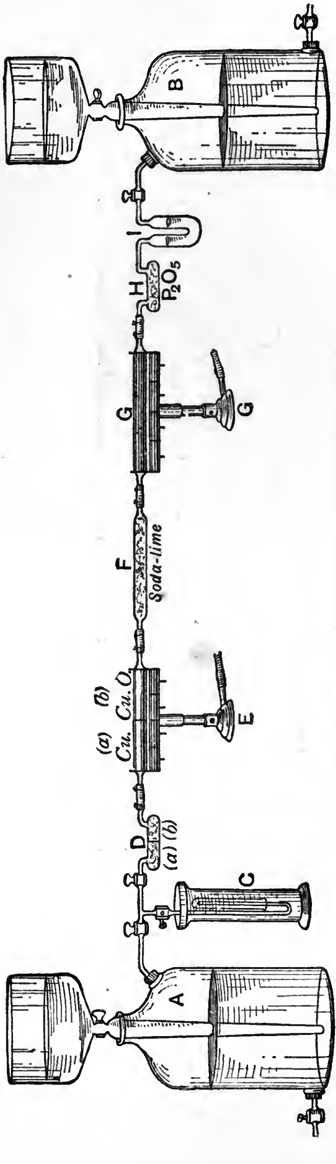


FIG. 307.—Ramsay's Method for the Preparation of Argon.

The separation of atmospheric argon is now carried out on the technical scale, since the gas is in demand for filling metal-filament electric lamps. If these are vacuous, the metal filament (composed of tungsten) volatilises, and a black film is deposited on the inside of the bulb, which reduces the efficiency of the lamp by obscuring the light. If the lamp is filled with argon, the blackening of the bulb is considerably reduced. The argon is obtained by circulating air through a mixture of 90 parts of calcium carbide and 10 parts of calcium chloride, heated to 800° in iron retorts. The nitrogen and oxygen are absorbed, the latter as calcium cyanamide (p. 544), the former as calcium carbonate, and the residual gas, after passing over heated copper oxide to oxidise carbon monoxide (which is absorbed by potash), is dried. Argon is also obtained from the liquid oxygen left after the evaporation of liquid air, which contains about 3 per cent. of argon. The oxygen is removed from the gas obtained by evaporation, by passing over heated copper, or by a hydrogen flame, and the residual gas freed from nitrogen by heated carbide. Argon is also obtained by the fractionation of liquid air, *e.g.*, in the Claude apparatus, and the gas, containing about 87 per cent. of argon, used for filling lamps. Argon obtained by all these processes contains other inactive gases (*e.g.*, krypton) in traces.

Inactive gases are also evolved from hot-springs having their sources at great depths in the earth. The spring of Bourbon-Lancy evolves 16,000 litres of inactive gases per annum, of which 10,000 litres are helium (see below). The water of these springs is radioactive.

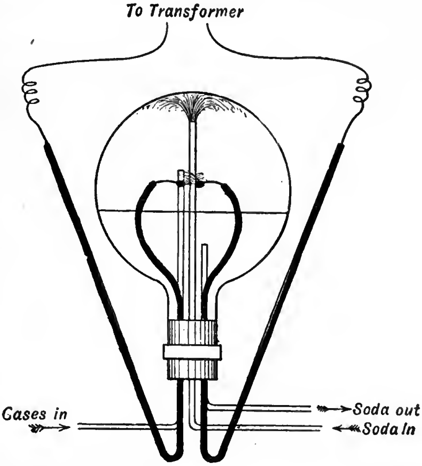


FIG. 308.—Rayleigh's Method for the Preparation of Argon.

In the residue from the evaporation of a large volume of liquid air Ramsay (1898) discovered two other new inactive gases, **krypton** (Greek *krypton*, concealed), and **xenon** (Greek *xenos*, the stranger). In crude liquid argon two other inactive gases, **helium**, and **neon** (Greek *neon*, new), were found. The latter was searched for in order to fill a gap in the periodic system (p. 471) between helium (4) and argon (40). Since helium is the element of least atomic weight in the group, the class of inactive elements may be called the **helium group.** They are most easily characterised by their **spectra,** in Geissler tubes. On prolonged exposure of the gas to the discharge, the light emitted by the tube diminishes in intensity. This is not due to absorption of the inert gas by the electrodes, but to removal of traces of nitrogen, etc., by the latter. In the absence of traces of diatomic gases, the inactive gases become fluorescent, or even non-conducting.

The examination of the residues from the evaporation of 120 tons of liquid air failed to indicate the presence of any other gases than those described.

Helium.—In 1868, the spectroscopic examination of the chromosphere of the sun during a total eclipse revealed the existence of a new yellow line, which did not exactly coincide with the D lines of sodium. Janssen called this line D_3, and Frankland and Lockyer concluded that it corresponded with an element not present in terrestrial substances, to which they gave the name **helium** (Greek *helios*, the sun). In 1894, Ramsay, at the suggestion of Miers, examined the gas evolved from *clèveite* (a variety of pitchblende), which had been supposed by Hillebrand (1888) to be nitrogen. This gas is evolved by heating the mineral with dilute sulphuric acid, or in a vacuum. It contains about 20 per cent. of nitrogen, but when this is removed by sparking with oxygen over alkali, there is a residue, which was found by Crookes to give, among other lines, the D_3 line in the spectrum. The gas was the unknown element of Frankland and Lockyer.

Doubts having been cast on the homogeneity of the gas, Ramsay and Travers (1897) showed, by an exhaustive fractional diffusion, that it could be separated into a light fraction, showing all the properties of helium, and unaffected by further diffusion, and a heavier fraction containing argon.

Helium was afterwards discovered in traces in the atmosphere, in gases occluded in the rare mineral *bröggerite*, in the gases of mineral springs (Cauterets, Bath, etc.), and especially in the natural gas from different localities in Kansas, U.S.A., some specimens of which contain more than ·1 per cent. by volume of helium. It has been prepared in large quantities from this natural gas, and, on account of its non-inflammable character, proposed for use in filling airships.

Helium occurs in small quantities in numerous minerals, and there is a good deal of evidence that its presence is the result of **radioactive changes** which have taken place at remote periods (p. 1034). The gas, although present only in minute quantities in the atmosphere (1 vol. in 250,000), may be separated by a slight modification of the Claude rectifier (p. 177) for the treatment of liquid air.

Helium is readily **purified** from other gases by making use of the discovery of Dewar (1904) that cocoanut charcoal at the temperature of liquid air completely absorbs all gases except hydrogen, helium, and neon. Quartz at a temperature of 1100° is permeable only to hydrogen and helium.

Liquid helium was first obtained by Kamerlingh Onnes in 1907, by the free expansion of the gas, previously cooled to 15° abs.; The liquid has a density of only 0·122, and has a very flat meniscus, indicating a small surface-tension. It boils at 4·3° abs.; by the rapid evaporation of the liquid, **solid helium** was obtained, and the temperature reduced to 1·5° above the absolute zero. At this temperature the electrical resistance of metals practically vanishes, so that a current set up by magnetic induction in a closed ring of the metal, cooled in liquid helium, continues to circulate for several days.

Other inactive gases.—Neon occurs in traces in the air (1 vol. in 55,000); it is separated by fractionation, but more readily by Dewar's method.

The inert gases are brought in contact with charcoal at − 100°, when the argon, krypton, and xenon are completely absorbed. The residual helium and neon are pumped off, and brought in contact with charcoal cooled to −185°; the neon is absorbed, and the helium (with a little neon) can be pumped off. On warming the charcoal, the **neon** is expelled. If the first charcoal bulb is now warmed to —80°, pure **krypton** is evolved; at higher temperatures, a mixture of krypton and xenon comes off. This gas is recondensed on charcoal at −150°, and the bulb put in connection with a second charcoal bulb cooled to −180°; the krypton passes over, leaving **xenon** in the first bulb. The gases are separated from the respective bulbs by warming (Valentiner and Schmidt, 1905). In a Geissler tube (p. 193), neon gives a beautiful orange-pink light; the same light is seen if a tube of neon at atmospheric or lower pressure, containing mercury, is shaken in a dark room (Collie). Neon is obtained from the residues of the Claude air liquefiers; a machine making 50 cu. m. of oxygen per hour produces 100 litres of neon per day. The gas is used for filling electrodeless vacuum lamps.

Another element of the group of inactive gases is **niton**, the emanation of radium: this will be considered in Chapter LI.

Properties of the helium group.—Since the inactive elements are devoid of all chemical affinities, they are completely described by an enumeration of their **physical properties**, given in the following table. Although niton may appear to be an intensely active substance, this is really due to its atomic disintegration; in itself it is a perfectly inert gas.

	Helium.	Neon.	Argon.	Krypton.	Xenon.	Niton.
Normal density	0·1786	0·9002	1·7818	3·708	5·851	9·97
Atomicweight (H = 1)	3·97	20·0	39·6	82·26	129·2	220·6
Critical temperature (abs.)	5°	60°	150·6°	210·5°	289·6°	377·5°
Critical pressure (atm.)	2·75	29	47·97	54·3	58·2	62·5
Boiling point (abs.)	4·5°	27·1°	86°	122°	163·9°	211°
Melting point (abs.)	—	—	83·4°	104°	133°	202°
Compressibility (p. 148)	±0	−0·00105	+0·00081	+0·00210	+0·00690	—
Absorption coeff. in water at 0°	0·0134	0·0114	0·0561	0·1207	0·2189	0·5
Ratio of specific heats, γ.	1·652	1·642	1·65	1·689	1·666	—

A uniform **gradation** is apparent in many of these properties; this, however, is broken in the case of neon with the compressibility, and solubility. The monatomic character of the gases is indicated by the values of the ratio of the specific heats, and is confirmed by other lines of evidence (*e.g.*, the refractive indices).

The inactive gases form a separate group in the Periodic System, and in conformity with the rule of valency (p. 463), this is called the **zero-group,** Group O. They bridge the gap between the strongly electropositive elements of the first group and the strongly electronegative elements of the seventh group (p. 471).

EXERCISES ON CHAPTER XXX

1. Give a brief account of the history of the discovery of the inactive gases. How is argon obtained from the air, and for what purpose is it used?

2. From what sources may helium be obtained? What possible use has been suggested for this gas?

3. How has the monatomic character of the inactive gases been established? What is their position in the periodic table?

4. Describe briefly how the different inactive gases may be separated from one another.

CHAPTER XXXI

PHOSPHORUS

The nitrogen group.—Group V. in the Periodic System comprises, besides radio-elements (Chapter LI), the following elements:

Odd series: nitrogen, phosphorus, arsenic, antimony, bismuth.

Even series: vanadium, niobium, tantalum.

Of these, all except nitrogen, phosphorus, and arsenic are **metals:** the non-metal nitrogen has been dealt with, and the other two non-metals, phosphorus and arsenic, are discussed in the present and following chapters. The metals are considered later.

The **properties of the elements of the odd series** are as follows:

	N.	**P.**	**As.**	**Sb.**	**Bi.**
Atomic weight (H = 1)	13·897	30·79	74·37	119·2	206·4
Sp. gr. of solid	0·79 (liq.)	1·83 (yellow) 2·20 (red)	5·73	6·62	9·80
Atomic volume	17·61	16·69 (yellow)	12·98	18·02	21·08
Melting point	—210°	44°	850°	630·0°	271°
Boiling point	—195·7°	287°	450° sublimes	1440°	1420°

The **typical compounds** of the elements, in which the latter are usually ter- or quinque-valent, but occasionally quadrivalent, are as follows:

NH_3, N_2H_4, N_3H NCl_3 N_2O, NO, N_4O_6, NO_2, N_2O_4, N_2O_5	PH_3, P_2H_4, $P_{12}H_6$, P_9H_2 PCl_3, PCl_5 P_4O_6, P_2O_4, P_4O_{10}	AsH_3 $AsCl_3$, $AsCl_5$ (?) As_4O_6, As_2O_5

SbH_3 $SbCl_3$, $SbCl_5$ Sb_4O_6, Sb_2O_4, Sb_2O_5	BiH_3 (?) $BiCl_3$ Bi_2O_3, Bi_2O_4, Bi_2O_5

The **hydrides** of these elements are all gaseous. Ammonia is a relatively strong base; phosphine (PH_3) is a very weak base, whilst arsine (AsH_3) and stibine (SbH_3) are devoid of basic properties. Bismuth forms a very unstable gaseous hydride, which dissolves in solutions of alkalies, and may be feebly acidic. The **oxides** of nitrogen are more numerous than those of the other elements, of which the types R_2O_3, R_2O_5, and sometimes R_2O_4 only are known. The **acidic character** of these oxides, *i.e.*, the electronegative character of the elements, diminishes from nitrogen to bismuth; from arsenic onwards the oxides also show basic properties: stable salts derived from Sb_2O_3, and Bi_2O_3, *e.g.*, $Bi(NO_3)_3$, are known. The **halogen compounds** of phosphorus are completely hydrolysed by water: $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$; those of arsenic can exist in presence of excess of acid: $AsCl_3 + 3H_2O \rightleftharpoons H_3AsO_3 + 3HCl$; those of antimony and bismuth are only partially hydrolysed: $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$.

Phosphorus.—About 1669, a physician of Hamburg, Brand, obtained a remarkable substance by distilling evaporated urine with sand and charcoal. It had the property of shining, the glow being visible in the dark, and was called **phosphorus** (Greek *phos*, light, and *phero*, I bear). Urine contains **microcosmic salt**, $NaNH_4HPO_4$; on heating, this yields **sodium metaphosphate**, $NaPO_3$, which is reduced on ignition with charcoal: $2NaPO_3 + 4C = Na_2CO_3 + 2P + 3CO$. The secret of the process was sold by Brand to Krafft; the latter exhibited the product in the Court of Charles II in 1677. Here it was seen by Boyle. The latter, and Kunckel in Berlin, independently rediscovered the method of preparation in the year 1678. Boyle called the substance *the noctiluca*, but it was generally known as "Boyle's," or "English," "phosphorus" to distinguish it from the Bolognian phosphorus (BaS, p. 877), which emitted a similar light, but only after previous exposure to sunlight. Scheele, in 1770, discovered calcium phosphate, $Ca_3(PO_4)_2$, in bones, and Gahn prepared phosphorus from bone-ash. The process formerly in use on the large scale (see below) for the preparation of phosphorus from bone-ash was devised by Scheele. The elementary nature of phosphorus was recognised by Lavoisier in 1777.

Occurrence of phosphorus.—Phosphorus occurs always in the combined state. The primary *mineral* appears to be *apatite*, $3Ca_3(PO_4)_2,CaF_2$; *chlorapatite*, $3Ca_3(PO_4)_2,CaCl_2$, also occurs. These are hard minerals, practically insoluble in dilute acids. From them, by weathering, the secondary deposits of phosphates have probably been formed, although many of these consist of fossil bones, in the formation of which the phosphates were first assimilated by animals. The so-called "soft phosphates" are *coprolites* (calcium phosphate of fossil excreta) and *Charleston phosphate* (27 per cent. P_2O_5), from river beds in South Carolina, and are easily decomposed by sulphuric acid. "Hard" varieties are *estramadurite* (33 per cent.

P_2O_5), *sombrerite* (35 per cent. P_2O_5), which are Spanish minerals, and *Redonda phosphate* (35–40 per cent. P_2O_5), a cheap and rich ore from the West Indies. The softer ores are used in the manufacture of phosphorus by the old process (*q.v.*), or of superphosphate; the hard varieties can be used in the modern electric furnace process for the preparation of the element. Phosphorus is an essential constituent of *vegetable and animal tissues*, occurring especially in the seeds, in the yolk of eggs, in the nerves and brain, and in bone-marrow, usually in the form of fats containing esters of phosphoric acid, known as *lecithins*, or *glycerophosphates*.

In the processes of tissue-metabolism, the organic phosphoric esters (*lecithins*) are broken up, and the phosphoric acid is excreted, through the agency of the kidneys, in the form of microcosmic salt. In order to repair the tissue-waste and to provide phosphates for the structure of bones, phosphorus compounds must form essential constituents of foods. Plants take up the element from the soil in the form of calcium phosphate, which dissolves in water containing carbonic acid. Phosphates, such as bone-meal, or superphosphates (p. 849), are therefore valuable fertilisers. The natural phosphates in the soil are probably derived from the weathering of apatite.

Phosphorus occurs in an inorganic form in the *bones*, which in the fresh condition contain about 58 per cent. of **calcium phosphate**, $Ca_3(PO_4)_2$, together with some calcium carbonate, fats, and organic matter containing nitrogen. The fat is extracted by solvents such as carbon disulphide, or chlorinated acetylenes (p. 680), and when the degreased bones are boiled with water under pressure in autoclaves, much of the remaining organic matter is dissolved. On evaporating the solution, **glue** is obtained. If the solid residue of the bones is now heated strongly out of contact with air, in iron retorts, the remaining organic matter is decomposed, and **animal charcoal** (p. 668) remains, which is used in decolorising sugar syrup. When it is no longer active, it is calcined in the air, when the carbonaceous matter is burnt off, and a white mass of **bone-ash** is left, consisting of about 83 per cent. of calcium phosphate, with calcium carbonate and a little fluoride.

Preparation of phosphorus.—Phosphorus was formerly prepared by Scheele's process from bone-ash, or soft mineral phosphates. These were decomposed by hot sulphuric acid (sp. gr. 1·5–1·6), so as to form insoluble calcium sulphate and phosphoric acid. The phosphoric acid solution was filtered off, evaporated to a syrup, mixed with powdered coke, and distilled in fireclay retorts at a white heat:

$Ca_3(PO_4)_2 + 3H_2SO_4 \rightleftharpoons 3CaSO_4 + 2H_3PO_4$ (**orthophosphoric acid**).
$H_3PO_4 \rightleftharpoons H_2O + HPO_3$ (**metaphosphoric acid**; formed on heating).
$4HPO_3 + 12C = 2H_2 + 12CO + P_4$ (**phosphorus**).

The phosphorus distilling over was condensed under water.

Practically all the phosphorus is now made by a method proposed by Wöhler (1829) in the **electric furnace** (Readman, Parker, and Robinson process, 1888). This method is applicable to hard, sparingly-soluble phosphates, since the mineral is not treated with acid. A mixture of phosphate, sand, and coke is fed by a worm-conveyor into a closed electric furnace, provided with an outlet above for the gases and phosphorus vapour, a slag hole below, and carbon electrodes between which an electric arc is struck (Fig. 309). The phosphate is decomposed at the high temperature by silica, which is very difficultly volatile and weakly acidic :

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5 \text{ (at 1150°)}.$$

The calcium silicate forms the molten slag. The vapour of phosphorus pentoxide is reduced by the carbon at about 1500°, forming carbon monoxide and phosphorus vapour, which pass out at the top : $P_2O_5 + 5C = 2P + 5CO$. About 5 kilowatt-hours are used per gram of phosphorus : the yield is 80–90 per cent. The cooled gas is passed into water, when crude phosphorus condenses as a dark-coloured mass. It is **purified** by melting under a solution of chromic acid, when some of the impurities are oxidised and pass into solution, and others are separated and rise as a scum. The liquid phosphorus may also be filtered by pressing through chamois leather. The colourless phosphorus is finally cast into wedges (about 2 lb.) in tin moulds, or into sticks, by running the liquid into glass tubes cooled in water, and drawing out the stick at the other end.

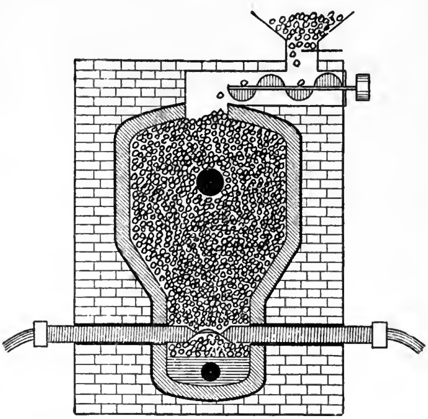


FIG. 309.—Electric Furnace for Manufacture of Phosphorus.

The annual production of phosphorus amounts to about 5,000 tons, most of it being used in the manufacture of matches. Some phosphorus is used in making phosphor-bronze, as a poison for rats, and in the preparation of phosphorus trichloride, pentachloride, and pentoxide, in chemical industries and laboratories.

EXPT. 245.—Mix 1 gm. of powdered sodium metaphosphate (obtained by heating microcosmic salt in a platinum crucible) with 0·5 gm. of aluminium powder and 3 gm. of fine white sand. Heat the mixture strongly in a hard glass tube in a current of dry hydrogen. Phosphorus distils over, condensing in the cool part of the tube. White fumes with a strong smell of phosphorus escape from the exit tube, which dips under water.

White (or yellow) phosphorus.—Ordinary **white phosphorus**, made as described, is a translucent white solid, like wax. It is soft enough at the ordinary temperature to be cut with a knife—an operation which should always be performed under water. Phosphorus is kept in bottles under water on account of the ease with which it takes fire in air. Below 5·5° the phosphorus becomes brittle, and the crystalline structure produced on cooling may be seen by etching the stick of phosphorus in concentrated nitric acid.

The specific gravity of white phosphorus is 1·82, and its melting point under water is 43·3°. In dry glass tubes it melts at 30°. The liquid exhibits supercooling. Phosphorus boils at 269° (various temperatures, from 269° to 290°, have been recorded, the discrepancies being probably due to the partial conversion of fused phosphorus into the red variety above 200°), yielding a colourless vapour, the density of which, between 512° and 1000°, corresponds with the formula P_4. Between 1500° and 1700° the density decreases, indicating partial dissociation: $P_4 \rightleftharpoons 2P_2$. According to Stock, the dissociation is 1 per cent. at 800°, and more than 50 per cent. at 1200°.

White phosphorus is very sparingly soluble in water (1 in 300,000), but dissolves in benzene, turpentine, olive oil, sulphur chloride, phosphorus trichloride, and especially in carbon disulphide (9 parts of P in 1 part of CS_2). From the elevation of the boiling point of the latter solvent, Beckmann found the molecular formula P_4, agreeing with that of the vapour, and Hertz obtained the same result from the depression of freezing point of benzene. On evaporation out of contact with air, the solution in carbon disulphide deposits large, transparent, regular crystals, usually rhombdodecahedra, which exhibit a play of colours resembling that of the diamond. These crystals may also be formed by the slow sublimation of phosphorus in an evacuated tube, one end being kept cool by a moist cloth; the tube is preserved in the dark, since on exposure to light the crystals become red and opaque. By shaking melted phosphorus under a cold solution of urea, it is obtained in the form of a fine powder. White phosphorus dissolves in cold concentrated nitric acid, forming phosphoric acid (*q.v.*).

The characteristic property of white phosphorus is the ease with which it undergoes oxidation when exposed to the air at the ordinary temperature, the spontaneous oxidation being accompanied with a green glow, or **phosphorescence.** If gently warmed to about 34°, it catches fire in dry air, and burns with a brilliant white light, forming white fumes of the pentoxide, P_2O_5. Finely-divided phosphorus takes fire spontaneously in the air. It may be burnt under water in a current of oxygen.

Expt. 246.—Place a few pieces of phosphorus in a test-tube supported in a beaker of water. Half fill the test-tube with water, and pass through a current of oxygen. Now heat the water in the beaker. When the temperature reaches 60° the phosphorus takes fire and burns under water where it comes in contact with the oxygen.

Expt. 247.—Pour a solution of phosphorus in carbon disulphide on a piece of blotting-paper supported on a tripod stand. The solvent rapidly evaporates, and the finely-divided phosphorus left catches fire and burns with the formation of fumes of P_2O_5. The paper is charred, but does not burn, since phosphoric acid, formed from the oxide by moisture in the air, is readily fusible, and protects the paper from contact with the air. For the same reason it is difficult to ignite a piece of paper in a phosphorus flame. The solution in ether exhibits phosphorescence when poured on hot water, or rubbed on the skin.

Sticks of white phosphorus kept under water become covered with a white crust, which may be an allotropic modification, or an oxide, since, according to Baudrimont, it is not formed in water free from air. This crust slowly turns red, and finally black, and the dark colour spreads through the mass of the phosphorus.

White phosphorus is very **poisonous**, the lethal dose being about 0·15 gm. Workmen exposed to the vapour are liable to decay of the bones, especially of the jaw (" phossy-jaw "), and its use in the manufacture of matches has been prohibited in many countries.

Red phosphorus.—This modification, formerly called " amorphous phosphorus," was prepared by Schrötter in 1845 by heating white phosphorus for a few hours at 250° in a flask filled with nitrogen or carbon dioxide. The liquid deposits a red powder, and finally solidifies to a purplish-red mass. The transformation begins at about 230° ; it is fairly rapid at 250°, and at higher temperatures becomes reversible. Considerable amounts of heat are evolved: P (white) = P (red) + 3·7 kgm. cal.

Red phosphorus is also left as a residue when white phosphorus burns in air, or in oxygen under water, and was, until Schrötter's discovery, considered to be a sub-oxide.

Expt. 248.—Heat a little white phosphorus in a strong sealed glass tube suspended by a wire in the vapour of diphenylamine boiling, at 310°, in a glass jacket (Fig. 310). The clear liquid deposits red phosphorus and slowly solidifies.

Brodie (1853) showed that the transformation of white into red phosphorus is considerably accelerated by the presence of a little iodine, and then occurs at 200°. The same change occurs when a little iodine, or selenium, is added to a solution of white phosphorus in carbon disulphide.

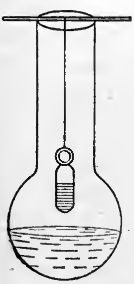


FIG. 310.—Conversion of White into Red Phosphorus.

Red phosphorus is manufactured by heating about a ton of phosphorus in a large cast-iron pot provided with a cover, through which passes an upright iron tube about 6 ft. long and 1 in. in diameter. The pot is carefully and uniformly heated to 240–250°, the temperature of the fused phosphorus being controlled by thermometers, protected by iron tubes, since phosphorus attacks glass. A little phosphorus burns, absorbing the oxygen from the air in the vessel, and oxidation then ceases. The hard solid left in the pot when the conversion is complete is ground up under water, and boiled with a solution of caustic soda to free it from unchanged white phosphorus (p. 618). It is then repeatedly washed with hot water and dried with steam. It contains about 0·5 per cent. of white phosphorus, and some phosphoric acid.

Red phosphorus has a density of 2·25. It is not self-luminous, has no taste or smell, and is not poisonous. On exposure to air, very little change occurs, although slight oxidation takes place, the dry powder becoming moist and phosphoric acid being formed. The powder does not ignite in the air until heated to about 240°. The melting point of red phosphorus is between 500° and 600°; when strongly heated it is converted into vapour, which on cooling deposits white phosphorus.

EXPT. 249.—Place a small heap of red phosphorus near one end of a flat piece of tinplate, and a small piece of white phosphorus at the other end. Support the tinplate on a tripod stand, and heat the end near the red phosphorus with a small Bunsen flame. The white phosphorus catches fire first, although it is further from the flame than the red phosphorus. The latter has, therefore, a higher ignition point.

EXPT. 250.—Place a little red phosphorus in a hard glass test-tube, fitted with a rubber stopper and two tubes. Displace the air from the tube by a slow stream of carbon dioxide, and heat the phosphorus strongly. Colourless drops of white phosphorus distil on to the cooler portion of the tube.

White phosphorus appears to be an unstable form: it passes slowly into red phosphorus, even at the ordinary temperature when exposed to light. The vapour pressure of white phosphorus at 200° is greater than that of red phosphorus at 350°, and if white phosphorus is placed in one limb of a U-tube at 324°, and red phosphorus at 350° in the other, distillation occurs from the cooler to the hotter position.

Allotropic forms of phosphorus.—Besides ordinary white phosphorus, or **α-white phosphorus,** two other white forms have been described. **β-white phosphorus** is formed by cooling the α-form to $-76{\cdot}9°$, or by subjecting it to about 12,000 atm. pressure: it crystallises in the hexagonal system. Vernon described another form, **γ-white phosphorus,** m.-pt. 45·3°, sp. gr. 1·827, obtained in rhombic prisms by cooling liquid phosphorus very slowly.

Scarlet phosphorus was obtained by Schenck by boiling a 10 per cent. solution of white phosphorus in phosphorus tribromide for ten hours. It deposits as a fine scarlet powder, more active than red phosphorus, but differing from white phosphorus in not oxidising in the air or being poisonous. For the latter reason, it is now used in the manufacture of matches. It dissolves in alkalies, evolving phosphine (*q.v.*), and turning dark in colour. Prepared as above, it always contains tribromide, but may be obtained pure by heating the tribromide with mercury at 240°: $2PBr_3 + 3Hg = 3HgBr_2 + 2P$.

Metallic phosphorus, or **α-black phosphorus,** is formed (Hittorf, 1865) by heating ordinary red phosphorus in a sealed tube at 530°, the upper portion of the tube being kept at 444°. Brilliant, opaque, monoclinic, or rhombohedral, crystals, sp. gr. 2·316 or 2·34, which do not oxidise in air, sublime. These crystals are also formed by dissolving phosphorus in lead at 400° in a closed tube, allowing it to crystallise, and dissolving out the lead with dilute nitric acid. This modification is not a conductor of electricity.

β-black phosphorus, sp. gr. 2·69, m.-pt. 587·5°, is formed irreversibly from white phosphorus at 200° under a pressure of 12,000 kgm. per sq. cm. It does not ignite at 400° in air, and is a fairly good conductor of electricity.

Violet phosphorus is formed by heating white phosphorus with a trace of sodium to 200° under very high pressure. It is crystalline, sp. gr. 2·35, m.-pt. 589·5°.

Red phosphorus was long considered to be amorphous, but Pedler and Retgers, in 1890, showed that it consists of small rhombohedral crystals. It is not considered to be a definite modification of phosphorus, since its properties (*e.g.*, heat of combustion) are variable, but is supposed to consist of a solid solution of scarlet phosphorus in metallic phosphorus. Some white phosphorus may also be present. It is insoluble in carbon disulphide, and is a feeble conductor of electricity. Whereas white phosphorus ignites spontaneously in chlorine, red phosphorus burns in the gas only when heated.

The glow of phosphorus.—The spontaneous oxidation of phosphorus, which takes place when white phosphorus is exposed to air, is accompanied by the emission of a faint green glow, white fumes being at the same time evolved. The glow is produced when only minute traces of phosphorus or oxygen are present, and its formation is used as a test for free phosphorus, when the latter is suspected in cases of poisoning.

Expt. 251.—A small piece of phosphorus is added to water in a flask connected with a Liebig's condenser (Fig. 311). On boiling the water, the phosphorus distils over with the steam, and a phosphorescent glow is seen in a dark room at the point in the condenser where the vapours deposit liquid.

Expt. 252.—The glow of phosphorus is strikingly shown in the following experiment, due to Smithells ("the cold flame"). A few pieces of phosphorus are placed in a receiver, which is then filled up with glass wool. The receiver is heated gradually on a water-bath, a stream of carbon dioxide being passed through (Fig. 312). The phosphorus vapour carried along with the gas oxidises in the air, and a green flame appears at the top of the exit tube. This is so cool that the hand may be held in it, and it will not kindle the head of a match.

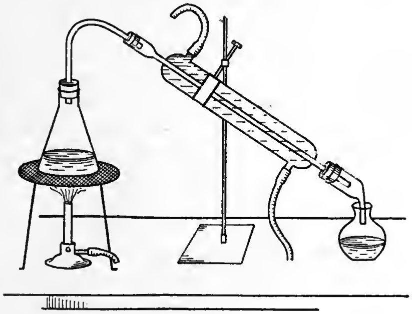


Fig. 311.—Detection of Phosphorus.

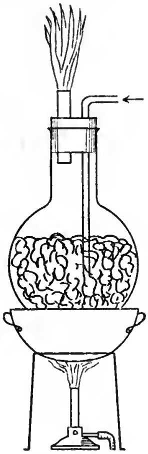


Fig. 312.—Smithells' "Cold Flame."

The glow of phosphorus was investigated by Boyle, who found that: (1) phosphorus glows only in the presence of air; (2) an acid is produced which differs from phosphoric acid, since it gives little flashes of light on heating [phosphorous acid]; (3) the glow is exhibited by solutions of phosphorus in olive, and some other, oils, but oils of mace and aniseed prevent it; (4) a very small quantity of phosphorus (1 part in 500,000 parts of water) can be detected by the glow; (5) after exposure to phosphorus, the air acquires a strong odour [ozone], distinct from the visible fumes.

Although a large number of other investigators have since examined the glowing of phosphorus, it cannot be said that any great advance has been made from the facts ascertained by Boyle in the seventeenth century. A little later than Boyle, Lemery, Slare, and Hawkesbee observed that the glow is brighter when the air is rarefied by an air-pump, although Lampadius showed that it is extinguished in a Torricellian vacuum, so that the presence of a trace of oxygen is necessary. The dependence of the glow on the pressure of the gas was exhibited in the most striking manner by Henry and by Graham, who made the remarkable observation that it ceases altogether in pure oxygen at atmospheric pressure, but reappears when the pressure is reduced or an indifferent gas added. This may be exhibited by the apparatus shown in Fig. 313. A stick of phosphorus is placed in the constricted part, *a*, of a tube containing oxygen confined over mercury, the levelling tube being adjusted so that the gas is at atmospheric pressure. No glow can be observed in the dark. If the levelling tube is now lowered so as to reduce the pressure, the phosphorus begins to glow. In oxygen at atmospheric pressure, phosphorus begins to glow at 25° ; the glow is very bright at 36°, and the phosphorus then very easily inflames. The following experiment

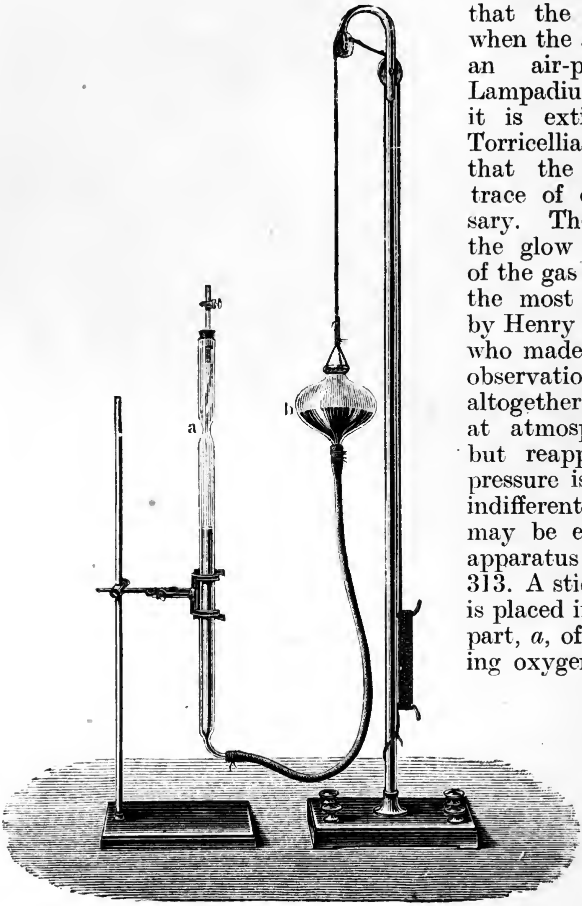


FIG. 313.—Effect of Pressure on Phosphorescence in Oxygen.

is more convenient, as there is then no danger of the phosphorus taking fire.

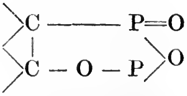
Expt. 253.—Heat a piece of phosphorus with olive oil in a flask on a water-bath. Cool the solution, and pour it into a round litre flask fitted with a rubber stopper carrying two gas delivery tubes. Displace the air from the flask by a current of dry oxygen. The glow ceases. Close one tube with a piece of rubber tubing and a clip, and connect the other with an air-pump. On reducing the pressure of the oxygen the glow commences again.

In perfectly dry oxygen phosphorus may be distilled without change.

Graham (1829) found that the glow of phosphorus is inhibited by the presence of ether, naphtha, or turpentine vapour. (The action of essential oils had been observed by Boyle.) One part of turpentine vapour in 4444 parts of air was sufficient. Later, observers found that many essential oils, camphor, naphthalene, carbon disulphide, and especially iodobenzene, had the same effect.

Schönbein (1848) considered that the glow is intimately related to the formation of *ozone* (p. 320), since (1) essential oils which destroy or dissolve ozone inhibit the luminosity; (2) at low temperatures no ozone is formed and phosphorus does not glow; (3) at 25° the production of ozone is a maximum, and the glow is brightest. The exact relation between the glow and the production of ozone is not yet settled.

The reaction occurs between phosphorus *vapour* and oxygen, since it is brighter at lower pressures, and an indifferent gas (N_2 or H_2), when passed over phosphorus, glows when mixed with oxygen. Some chemists think oxygen atoms are formed: $P_4 + 6O_2 = 2P_2O_5 + 2O$; $O_2 + O = O_3$. Thorpe considers that part at least of the glow is due to the oxidation of the lower oxide, P_4O_6, which is also formed, and this is supported by Schenck. The latter considers that the lower oxide, when formed, reacts with water to form phosphorus, phosphorous acid, phosphoric acid, and solid hydrogen phosphide, $P_{12}H_6$ (p. 622). The air also becomes ionised, *i.e.*, it conducts electricity, and this is sometimes considered to be due to an "emanation" given out by the phosphorus. The action of essential oils in stopping the glow is supposed to be due to the absorption of the P_4O_6 by the double linkages in the compounds, with formation of rings:



This explanation cannot, however, cover all the cases.

The extinction of the glow in pure oxygen is put down to the oxidation of P_4O_6 to phosphoric acid.

Hydrogen phosphides.—Phosphorus forms with hydrogen four compounds :

PH_3, **Trihydrogen phosphide** (*gaseous phosphoretted hydrogen ; phosphine*), m.-pt. − 133°, b.-pt. − 85°.

P_2H_4, **Dihydrogen phosphide** (*liquid phosphoretted hydrogen*), m.-pt. −10°, b.-pt. 57°.

Two varieties of **solid phosphoretted hydrogen,** $P_{12}H_6$ and P_9H_2.

Trihydrogen phosphide, usually known as **phosphine,** or *phosphoretted hydrogen,* was obtained by Gengembre, in 1783, by boiling white phosphorus with a solution of caustic potash. Caustic soda, lime, or baryta may also be used. The colourless gas so obtained has a very unpleasant odour of rotten fish, and is poisonous. It is spontaneously inflammable in air, and its production from decaying organic matter in marshes is supposed to be responsible for the phenomenon known as the *Will-o'-the-wisp.* In the above reaction phosphine and an acid salt of **hypophosphorous acid,** H_3PO_2, *e.g.*, sodium hypophosphite, NaH_2PO_2, are formed :

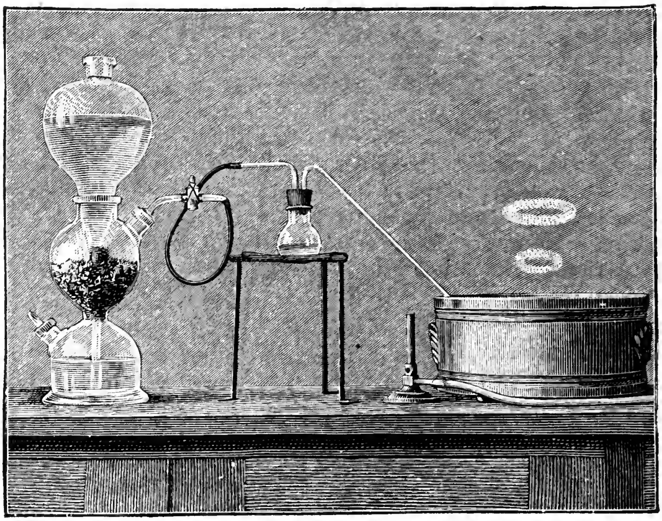


FIG. 314.—Preparation of Phosphine.

$$P_4 + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

The hypophosphite, on boiling, is partly decomposed, with liberation of hydrogen, so that the gas is not pure: $NaH_2PO_2 + 2NaOH = 2H_2 + Na_3PO_4$ (sodium phosphate) ; baryta gives a purer gas. Hydrogen is also evolved by the direct reaction : $2P + 2NaOH + 2H_2O = 2NaH_2PO_2 + H_2$.

EXPT. 254.—Pieces of white phosphorus are placed in a flask (Fig. 314) containing a 30–40 per cent. solution of caustic soda. The air is first swept out by a current of hydrogen or coal gas, to avoid the explosion which would occur by the spontaneous ignition of a mixture of phosphine and air, and the flask is heated. Each bubble of phosphine which escapes from the delivery tube dipping under water ignites spontaneously with a bright flash, and a vortex-ring of white smoke, consisting of phosphorus pentoxide, rises in the air. The experiment is best performed in a fume-cupboard.

Small quantities of phosphine appear to be produced by heating red phosphorus in hydrogen, or by adding bits of white phosphorus to a mixture of zinc and dilute sulphuric acid evolving hydrogen (nascent hydrogen). The hydrogen then burns with a green flame. This is a delicate test for free phosphorus. The result may be due to phosphorus vapour.

The spontaneous inflammability of the gas prepared by Gengembre's method is due to the presence of traces of the liquid hydride, P_2H_4: $6P + 4NaOH + 4H_2O = 4NaH_2PO_2 + P_2H_4$.

Davy showed that phosphine is evolved on heating **phosphorous acid,** H_3PO_3 (obtained by the action of water on phosphorus trichloride); this gas is not spontaneously inflammable, but ignites at 100°: $4H_3PO_3 = 3HPO_3 + 3H_2O + PH_3$.

P. Thenard, in 1845, showed that if the spontaneously inflammable gas is passed through a tube immersed in a freezing mixture, the liquid hydride is deposited, and the gas is no longer spontaneously inflammable. The same result is obtained by passing the gas over recently ignited charcoal, which absorbs the vapour of the dihydride, or by mixing the gas with a little ether vapour. The pure gas becomes spontaneously inflammable if mixed with a little vapour of fuming nitric acid.

A gas which is not spontaneously inflammable, but contains hydrogen as impurity, is formed if phosphorus is heated with alcoholic potash.

Pure phosphine is prepared by heating phosphorous acid, by warming phosphonium iodide (*q.v.*) with caustic potash solution: $PH_4I + KOH = KI + H_2O + PH_3$, or by the action of dilute sulphuric acid on aluminium phosphide (prepared by heating aluminium powder and red phosphorus). It is sparingly soluble in water, alcohol, or ether.

The **normal density** of phosphine is 1·52058 gm./lit. It is decomposed by electric sparks, depositing red phosphorus, and increasing in volume in the ratio 2 : 3 :—$2PH_3 = 2P + 3H_2$. In this way its composition is determined. The gas is also decomposed by heating to 440°.

If phosphine is kindled in a test-tube, it burns with deposition of phosphorus: the heat of combustion of part of the gas decomposes the rest (*cf.* H_2S). A mixture of pure phosphine with oxygen is not spontaneously explosive. but if the pressure is reduced, a violent explosion occurs (Labillardière, 1817).

Phosphine ignites spontaneously in chlorine. It combines with many metallic chlorides. The pure gas is completely absorbed by a solution of bleaching powder. It precipitates phosphides from solutions of many metallic salts (*e.g.*, $CuSO_4$, $AgNO_3$). These phosphides are also formed by heating the solutions with white phosphorus.

EXPT. 255.—Boil a few pieces of white phosphorus with a solution of copper sulphate. Black **cupric phosphide,** Cu_3P_2, is formed.

Phosphonium compounds.—Although phosphine has a neutral reaction to litmus paper, it is capable of acting as a feeble base, forming **phosphonium salts** with halogen hydracids: $PH_3 + HX = PH_4X$, analogous to ammonium salts, NH_4X. A mixture of phosphine and dry hydrogen chloride does not react at atmospheric pressure, but if cooled to $-35°$, or compressed to 18 atm. at 15°, it deposits white crystals of **phosphonium chloride,** which dissociate again on warming or on reducing the pressure: $PH_3 + HCl \rightleftharpoons PH_4Cl$. **Phosphonium bromide,** PH_4Br, is more stable, and is produced in cubic crystals when a mixture of PH_3 and HBr is led into a moderately cooled flask. **Phosphonium iodide,** PH_4I, is a fairly stable compound, and is formed on mixing PH_3 and HI at the ordinary temperature and pressure. It dissociates at 30°, but the crystals can be sublimed. Phosphonium iodide is most conveniently prepared by the following process.

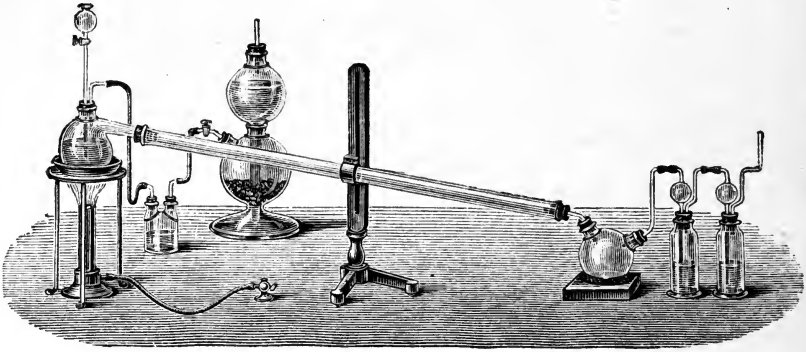


FIG. 315.—Preparation of Phosphonium Iodide.

EXPT. 256.—One hundred parts of white phosphorus are dissolved in an equal weight of carbon disulphide in a tubulated retort, from which the air has been removed by a current of dry carbon dioxide. One hundred and seventy-five parts of iodine are then added, and the carbon disulphide is distilled off on a water-bath in a current of CO_2. The neck of the retort is then connected with a wide glass tube and receiver, and, by means of a dropping-funnel fitted in the tubulure of the retort, 85 parts of water are dropped gradually on to the phosphorus iodide (Fig. 315). Phosphonium iodide sublimes into the wide tube; the retort is gently warmed at the end of the process. Two wash-bottles containing water are attached to the receiver, to absorb the hydriodic acid evolved: $9P + 5I + 16H_2O = 4H_3PO_4 + 5PH_4I$.

Phosphonium iodide is at once decomposed by water or alkalies, evolving pure phosphine: $PH_4I + Aq. = PH_3 + HIAq.$

Liquid phosphoretted hydrogen, P_2H_4.—This substance is prepared by the action of warm water on calcium diphosphide: $Ca_2P_2 + 4H_2O = 2Ca(OH)_2 + P_2H_4$.

Calcium phosphide, Ca_2P_2, is formed as a dark brown solid, containing Ca_3P_2 and the pyrophosphate, $Ca_2P_2O_7$, by passing phosphorus vapour over fragments of quicklime strongly heated in a hard glass tube.

Tricalcium diphosphide, Ca_3P_2, is obtained in a pure state by heating calcium and phosphorus together under petroleum. It gives pure phosphine, not spontaneously inflammable, when treated with water.

EXPT. 257.—If pieces of calcium phosphide are dropped into warm water, gaseous phosphoretted hydrogen, PH_3, containing the vapour of the dihydride, P_2H_4, is evolved, and each bubble ignites spontaneously as it breaks on the surface of the water.

Tin canisters filled with calcium phosphide, attached to wooden floats, are sometimes used at sea for signalling. The canister is pierced above and below and thrown overboard. The gas ignites spontaneously and burns with a luminous flame (Holmes's signal).

In the preparation of liquid phosphoretted hydrogen, pieces of calcium phosphide are dropped through a wide tube into water at 60° in a Woulfe's bottle (Fig. 316), the air having been previously displaced by hydrogen. The gas is passed through a cooled tube

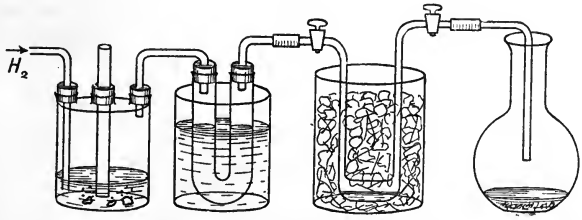


FIG. 316.—Preparation of Liquid Phosphoretted Hydrogen.

to deposit moisture, and the liquid phosphoretted hydrogen then condensed in a second tube cooled in a freezing mixture.

The empirical formula of liquid phosphoretted hydrogen is PH_2; the formula P_2H_4 is given to the substance by analogy with hydrazine, N_2H_4, although the vapour density cannot be found, since the vapour is too unstable. The liquid also decomposes on exposure to light; gaseous phosphine is evolved, and red **solid hydrogen phosphide**, $P_{12}H_6$, deposited: $15P_2H_4 = P_{12}H_6 + 18PH_3$. The same solid is formed if the uncondensed vapours from the preparation of the liquid are passed into a large flask containing a little fuming hydrochloric acid.

Solid hydrogen phosphides, $P_{12}H_6$ and P_9H_2.—The red solid hydride, prepared as described above, is found, from the depression of freezing point of white phosphorus in which it is dissolved, to be $P_{12}H_6$. When heated in a vacuous tube it evolves pure phosphine and leaves a second red solid hydride, P_9H_2: $5P_{12}H_6 = 6P_9H_2 + 6PH_3$. A third solid hydride, P_5H_2, is said to be formed by the action of very dilute acetic acid on the phosphides of alkali metals, *e.g.*, Na_2P_5 (p. 793).

By digesting white, or scarlet, phosphorus with alcoholic potash and water, a dark red solution is formed, which appears to contain **potassium polyphosphides,** K_2P_n. Phosphine is evolved, together with hydrogen, and hypophosphite is also formed. On acidifying the solution, a reddish-yellow precipitate, formerly considered to be a suboxide, P_4O, but probably impure solid hydrogen phosphide mixed with red phosphorus, is thrown down. $P_{12}H_6$ dissolves in alkalies to form red solutions, and forms a dark-coloured compound with piperidine, $P_{12}H_6(C_5H_{11}N)_3$. It therefore behaves as a weak acid.

Halogen compounds of phosphorus.—Phosphorus forms two series of **halogen compounds,** in which it is tervalent and quinquevalent, respectively: PX_3 and PX_5. These are obtained by the direct combination of phosphorus and the halogen, PX_3 or PX_5 being formed according as the former or the latter is in excess. The **physical properties** of these compounds (iodine also forms P_2I_4, analogous to P_2H_4) are given below:

PF_3, colourless gas, b.-pt. − 95°, m.-pt. − 160°.
PF_5, colourless gas, b.-pt. − 75_5°, m.-pt. − 83°.
PCl_3, colourless liquid, b.-pt. 76°, m.-pt. − 112°.
PCl_5, white, crystalline solid, sublimes: m.-pt. 148°, b.-pt. 162° in sealed tube
PBr_3, colourless liquid, b.-pt. 170·8°, m.-pt. − 41·5°.
PBr_5, orange-yellow, crystalline solid, decomposes on heating.
P_2I_4, orange-red crystals, m.-pt. 110°.
PI_3, dark red crystals, m.-pt. 55°.

The compounds PBr_7, PBr_2F_3, PCl_3Br_2, $PCl_3Br_2 \cdot Br_2$, etc., are also known.

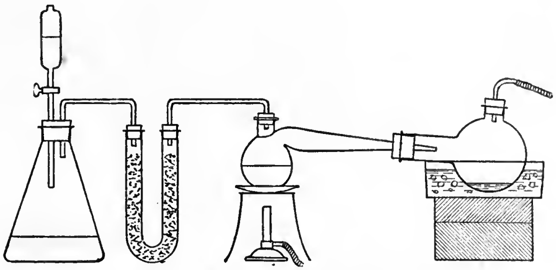


FIG. 317.—Preparation of Phosphorus Trichloride.

Phosphorus trifluoride, PF_3, is obtained by the action of arsenic trifluoride (*q.v.*) on phosphorus trichloride: $AsF_3 + PCl_3 = AsCl_3 + PF_3$; by warming phosphorus tribromide with zinc fluoride: $3ZnF_2 + 2PBr_3 = 2PF_3 + 3ZnBr_2$; or by heating copper phosphide with lead fluoride. The gas has no action on glass in the cold; it is hydrolysed by water: $PF_3 + 3H_2O = H_3PO_3 + 3HF$. The **pentafluoride,** PF_5, is formed when phosphorus burns in fluorine; when arsenic trifluoride is added to phosphorus pentachloride in a freezing mixture: $3PCl_5 + 5AsF_3 = 3PF_5 + 5AsCl_3$; or when phosphorus fluorbromide (obtained by cooling a mixture of bromine and PF_3 to − 20°) is warmed to 15°: $5PF_3Br_2 = 3PF_5 + 2PBr_5$. The density of the gas is normal, corresponding with the formula PF_5, and this confirms the quinquevalency of phosphorus. The gas does not attack glass, fumes in the air, forming POF_3, and combines directly with ammonia gas, forming a solid: $2PF_5,5NH_3$.

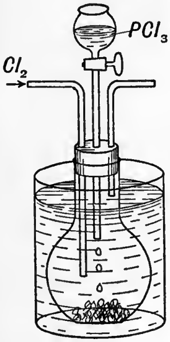


FIG. 318.—Preparation of Phosphorus Pentachloride.

Phosphorus trichloride, PCl_3 (Gay-Lussac and Thenard, 1808), is formed (along with some pentachloride) when phosphorus burns spontaneously in chlorine. It is made by passing a stream of dry chlorine over white or red phosphorus in a retort, and condensing the product in a dry cooled receiver (Fig. 317). It is purified by standing over white phosphorus, and redistilling. The pure liquid is colourless, and may be preserved in sealed flasks. The vapour density is normal. It fumes strongly in moist air: $PCl_3 + 3H_2O = 3HCl + H_3PO_3$ (phosphorous acid).

Phosphorus pentachloride, PCl_5 (Davy, 1810; Dulong, 1816), is prepared [EXPT. 258] by passing dry chlorine through a large cooled flask, into which the trichloride is allowed to drop from a tap-funnel (Fig. 318). It is a greenish-white solid, which sublimes at the ordinary pressure below 100° without previous fusion, the vapour being dissociated into trichloride and chlorine (p. 153): $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Above 300° the dissociation is practically complete. If heated under pressure, it melts at 148°. Although the compound is not, as was formerly supposed, a molecular compound PCl_3,Cl_2, two atoms of chlorine are very reactive, and many metals (Zn, Cd, and even Au and Pt) are converted into chlorides, PCl_3 being left: $PCl_5 + Zn = ZnCl_2 + PCl_3$.

Phosphorus tri- and penta-chlorides are violently hydrolysed by water, the reactions being irreversible (p. 450). The trichloride is completely freed from halogen, and phosphorous acid, H_3PO_3, is formed (with a small quantity of water, a trace of POCl is said to be formed): $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$. In the case of the pentachloride the reaction proceeds in two stages. With a little water, liquid **phosphorus oxychloride,** or **phosphoryl chloride,** $POCl_3$, is produced, which is further hydrolysed by excess of water with formation of **orthophosphoric acid,** H_3PO_4:

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$
$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

If excess of water is added to the pentachloride, phosphoric acid is produced, although the oxychloride is probably formed as an intermediate product: $PCl_5 + 4H_2O = 5HCl + H_3PO_4$.

Inorganic oxy-acids, organic acids (containing the **carboxyl** group, —CO·OH, p. 518), and alcohols (hydroxides of hydrocarbon radicals, *e.g.*, methyl alcohol, $CH_3 \cdot OH$), containing the **hydroxyl** group, OH, react with phosphorus tri- or penta-chloride, the hydroxyl group being eliminated and **substituted** by an atom of chlorine. This reaction is frequently applied in organic chemistry to the detection of hydroxyl groups in compounds:

$$\underset{\textbf{Ethyl alcohol}}{3C_2H_5 \cdot OH} + PCl_3 = \underset{\textbf{Ethyl chloride}}{3C_2H_5Cl} + H_3PO_3.$$

$$\underset{\textbf{Acetic acid}}{CH_3 \cdot CO \cdot OH} + PCl_5 = \underset{\textbf{Acetyl chloride}}{CH_3 \cdot CO \cdot Cl} + POCl_3 + HCl.$$

Acetone, $(CH_3)_2CO$, which does not contain a hydroxyl group, reacts with phosphorus pentachloride, but the oxygen atom alone is replaced by *two* atoms of chlorine:

$$\underset{\textbf{Acetone}}{(CH_3)_2CO} + PCl_5 = \underset{\textbf{Dichloropropane}}{(CH_3)_2CCl_2} + POCl_3.$$

Sulphur trioxide reacts violently with phosphorus trichloride: $SO_3 + PCl_3 = SO_2 + POCl_3$. Phosphorus pentachloride reacts with dry ammonia, forming ammonium chloride and **chlorophosphamide,** $PCl_3(NH_2)_2$. The latter is converted by water into **phosphamide,** $PO \cdot NH \cdot NH_2$, a white powder insoluble in water, dilute acids, and alkalies. If phosphamide is heated in absence of air, **phospham,** $(PN_2H)_x$, remains as a white powder, which is only very slowly oxidised on heating to redness in air. It is decomposed with incandescence by fused alkalies, ammonia and a phosphate being formed.

At 175–200°, ammonia and phosphorus pentachloride form a mixture of six **phosphonitrile chlorides**: $(PNCl_2)_3$, $(PNCl_2)_4$, $(PNCl_2)_5$, $(PNCl_2)_6$, $(PNCl_2)_7$, and $(PNCl_2)_x$, which are very stable. The main product is $(PNCl_2)_3$, b.-pt. 256°, m.-pt. 114°. Ethereal solutions of these compounds, when shaken with water, form **metaphosphimic acids**; stable salts, *e.g.*, $P_3N_3O_6H_3(NH_4)_3 + H_2O$, are known.

White phosphorus explodes in contact with bromine; liquid bromine dropped on red phosphorus in a cooled flask reacts with evolution of light, and the **tribromide,** PBr_3, distils over. By adding bromine to this, the solid **pentabromide** is formed. The latter is also formed by the action of bromine and iodine on the trichloride; iodine chloride is also formed: the reaction, $2PCl_3 + 3Br_2 \rightleftharpoons 2PBr_3 + 3Cl_2$, takes place to a slight extent, and the Cl_2 is removed by the iodine as fast as it is produced. The solid exists in two forms: a red variety obtained by rapidly cooling the vapour, and a yellow stable variety obtained on slow cooling. The vapour is dissociated: $PBr_5 \rightleftharpoons PBr_3 + Br_2$.

White phosphorus inflames in contact with iodine; if solutions of iodine and phosphorus in carbon disulphide are mixed, the **di-iodide** and **tri-iodide,** P_2I_4 and PI_3, are obtained on evaporation.

A **dichloride,** P_2Cl_4, corresponding with P_2I_4, is said to be formed, as an oily, fuming liquid, by the action of the silent discharge on a mixture of PCl_3 vapour and hydrogen.

Sulphides of phosphorus.—Yellow phosphorus and sulphur form spontaneously inflammable solid solutions when fused together, but if a mixture of red phosphorus and small pieces of roll sulphur is heated in a loosely-corked glass flask on a sand-bath, chemical reaction commences, and then proceeds without further heating. According to the proportions taken, the **sulphides** P_2S_5, P_4S_7, and P_4S_3 are obtained. The **pentasulphide** is purified by distilling in dry carbon dioxide; it is a pale yellow solid melting at 275° and boiling at 530°; the vapour has the normal density. The substance is rapidly hydrolysed by water:

$$P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S,$$

and is used in organic chemistry for replacing the hydroxyl group, OH, in compounds by the group SH. Thus, alcohol, C_2H_5OH, forms **mercaptan,** $C_2H_5 \cdot SH$. **Tetraphosphorus trisulphide,** P_4S_3, is purified by crystallisation from carbon disulphide or phosphorus trichloride, or by distillation *in vacuo*. It melts at 172·5°, boils at 408°, giving the normal vapour density, and is only slowly hydrolysed by water. P_4S_7 forms slightly yellow crystals from CS_2, m.-pt. 310°, b.-pt. 523°.

Matches.—Common **lucifer matches** are made by dipping thin strips of wood, cut by machinery and coated at one end with paraffin wax or sulphur, into a paste of yellow phosphorus, gum, red lead, and sometimes potassium chlorate. Bundles of splints are dipped at once, and then dried. The heads ignite when rubbed on sand-paper, the local heating bringing about combustion. On account of the poisonous properties of yellow phosphorus, it is being replaced by scarlet phosphorus (p. 614); the sulphide, P_4S_3, is also used. **Safety matches** are dipped into a paste of 24 parts of antimony sulphide, 32 of potassium chlorate, 12 of potassium dichromate, 32 of red lead, and gum. The heads contain no phosphorus. They are rubbed on a strip of paper coated with red phosphorus, antimony sulphide, powdered glass, and gum, attached to the box. They may also be ignited by drawing rapidly over glass or linoleum. The wood is often impregnated with borax, so that it does not glow after the flame is blown out.

Oxides and oxy-acids of phosphorus.—Three **oxides** and several **oxy-acids** of phosphorus are known:—

—	**Hypophosphorous acid,** H_3PO_2.
Phosphorus trioxide, P_2O_3 or P_4O_6.	**Phosphorous acid,** H_3PO_3.
Phosphorus tetroxide, P_2O_4.	**Hypophosphoric acid,** H_2PO_3
Phosphorus pentoxide, P_2O_5 or P_4O_{10}, the anhydride of three phosphoric acids.	**Phosphoric acids:** $P_2O_5 + 3H_2O = 2H_3PO_4$, **ortho-phosphoric acid**; $P_2O_5 + 2H_2O = H_4P_2O_7$, **pyro-phosphoric acid**; $P_2O_5 + H_2O = 2HPO_3$, **meta-phosphoric acid,** of which polymeric modifications, $(HPO_3)_n$, are known.
—	**Permonophosphoric acid,** H_3PO_5; **Perphosphoric acid,** $H_2P_2O_8$.

The so-called **phosphorus sub-oxide,** P_4O, is probably a mixture of red phosphorus and the solid hydride, $P_{12}H_6$ (p. 622). **Leverrier's oxide** (1838), obtained as a red powder by allowing sticks of phosphorus partly covered with phosphorus trichloride to stand in a flask of air, is probably red phosphorus.

The burning of phosphorus.—When phosphorus is burnt in a free supply of air, **phosphorus pentoxide,** P_2O_5, first observed by Boyle and called "flowers of phosphorus," is formed. During the later stages of the combustion of phosphorus in a limited supply of air, **phosphorus trioxide,** P_2O_3, is formed. The phosphorus is extinguished before all the oxygen is removed, and a portion of the phosphorus is converted into red phosphorus

Expt. 259.—Dry the air inside a tall bell-jar by means of a capsule of sulphuric acid standing on a ground glass plate supporting the jar. After a few hours remove the capsule, and replace it by a small porcelain crucible-lid supported on a cork, in which a bit of phosphorus is placed. The phosphorus is ignited by touching with a hot wire as it is placed under the jar. Notice the bright flame, and the formation of a snow-white powder (P_2O_5) which rapidly settles. After a time, the flame becomes larger, greenish, and flickering: P_2O_3 is then formed. Finally it goes out.

Phosphorus pentoxide, P_2O_5.—This oxide is always prepared by the combustion of phosphorus in air or oxygen. On a large scale, the apparatus shown in Fig. 319 is used.

The sheet-iron cylinder is provided with an opening at the side, through which a copper spoon containing phosphorus is introduced. The phosphorus is ignited, and the pentoxide produced settles out, and falls into the dry bottle below. More phosphorus is added from time to time by drawing out the spoon, and the lid is raised to renew the air.

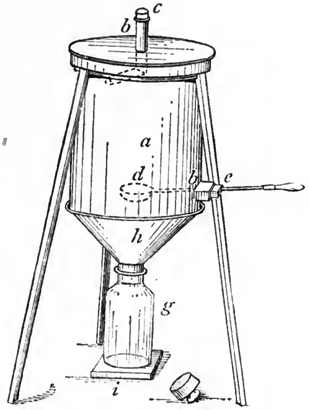


Fig. 319.—Preparation of Phosphorus Pentoxide.

The voluminous powder so obtained, when heated to 440°, becomes more compact and less volatile. If distilled in dry carbon dioxide, the pentoxide forms crystals subliming at 250°. The compact variety melts under pressure at a red heat, forming a vitreous mass.

Commercial phosphorus pentoxide contains some trioxide, P_2O_3, and metaphosphoric acid. It may be purified by volatilising in a current of oxygen in a hard glass tube, passing the gas over heated platinised pumice, and condensing in a cooled receiver. The following method is more convenient:

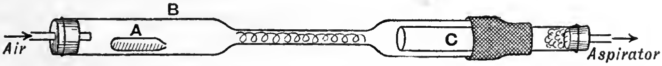


Fig. 320.—Preparation of Pure P_2O_5.

Dry red phosphorus is sealed up in a hard glass tube with a capillary tip, *A* (Fig. 320), placed in the hard glass tube, *B*. A slow stream of dry air is passed through *B*, and the part under the phosphorus heated till a small flame appears at the capillary. The narrow part of the tube *B*, containing a spiral of platinum wire, is heated to redness. The pentoxide is collected in the tube *C*, which is plugged with glass wool, and is withdrawn when filled.

The vapour density of phosphoric oxide at 1400° is slightly higher than corresponds with the formula P_4O_{10}, but since the molecular weight in the solid state is not known, the simpler formula P_2O_5 is generally used.

Phosphorus pentoxide exhibits a strong phosphorescence after illumination; the effect is more marked at low temperatures. Its most characteristic chemical property is its powerful affinity for water. The solid rapidly becomes moist and sticky on exposure to air, **metaphosphoric acid,** HPO_3, being formed, and it withdraws the last traces of moisture from gases dried with calcium chloride, caustic potash, or sulphuric acid. When thrown into water, phosphorus pentoxide dissolves with a hissing noise and the evolution of much heat (*cf.* SO_3, p. 498). Phosphorus pentoxide withdraws the elements of water from many acids, and other substances containing hydrogen and oxygen, forming anhydrides (*e.g.*, SO_3 from H_2SO_4, N_2O_5 from HNO_3, Cl_2O_7 from $HClO_4$). It may, in these reactions, continuously remove traces of water already produced by dissociation of the acids: this is undoubtedly the case with nitric and sulphuric acids: $2HNO_3 \rightleftharpoons N_2O_5 + H_2O$.

The phosphoric acids.—Phosphorus pentoxide is the anhydride of the **phosphoric acids,** three of which are known:

$$P_2O_5 + H_2O = 2HPO_3, \textbf{ metaphosphoric acid.}$$
$$P_2O_5 + 2H_2O = H_4P_2O_7, \textbf{ pyrophosphoric acid.}$$
$$P_2O_5 + 3H_2O = 2H_3PO_4, \textbf{ orthophosphoric acid.}$$

These may also be regarded as products of dehydration of a hypothetical acid, $P(OH)_5$: $P(OH)_5 - H_2O = H_3PO_4$; $2H_3PO_4 - H_2O = H_4P_2O_7$; $H_4P_2O_7 - H_2O = 2HPO_3$.

Metaphosphoric acid, HPO_3, is formed as a viscous mass when the anhydride is exposed to moist air, or moistened with cold water: $P_2O_5 + H_2O = 2HPO_3$. If a solution in water is boiled, metaphosphoric acid is converted into **orthophosphoric acid**:

$$HPO_3 + H_2O = H_3PO_4.$$

This change occurs slowly on standing in the cold, pyrophosphoric acid being formed as an intermediate product. The natural mineral phosphates, and bone-ash (p. 609), are salts of orthophosphoric acid, and this was the first phosphoric acid to be prepared. The fertiliser *guano*, consisting of the excreta of sea birds, is rich in phosphates, and also in combined nitrogen. Another source of phosphates, used for fertilisers, is the *basic slag*, $Ca_4P_2O_9$, of steel furnaces (p. 981).

When disodium orthophosphate, Na_2HPO_4, is heated to redness, it forms the sodium salt of pyrophosphoric acid :

$$2Na_2HPO_4 - H_2O = Na_4P_2O_7.$$

Orthophosphoric acid, H_3PO_4.—This acid is prepared technically by digesting 100 parts of bone-ash with a mixture of 96 parts of concentrated sulphuric acid and 1000 parts of water for several hours : $Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$. The calcium sulphate is filtered off, and the phosphoric acid evaporated to a specific gravity of 1·7 (85 per cent. H_3PO_4). The product is impure, containing acid calcium phosphate, $CaH_2(PO_4)_2$, which may be removed by adding concentrated sulphuric acid, filtering, evaporating, and driving off the volatile sulphuric acid by ignition. The fused mass on cooling solidifies to a glass of **metaphosphoric acid,** $(HPO_3)_n$, usually called *glacial phosphoric acid.* It contains a little magnesium phosphate.

Pure orthophosphoric acid is obtained by the oxidation of phosphorus with nitric acid. Oxides of nitrogen are evolved.

EXPT. 260.—Five gm. of red phosphorus are heated with 50 c.c. of concentrated nitric acid in a flask provided with a reflux condenser fitted with a ground glass stopper (Fig. 321). Red fumes of oxides of nitrogen are evolved, so that the experiment is performed in a fume-cupboard. When the phosphorus has dissolved, the liquid is evaporated in a platinum dish on a sand-bath, a little concentrated nitric acid is added to oxidise any phosphorous acid, and the liquid is then evaporated and heated to drive off nitric acid. The glassy residue is dissolved in water, and evaporated in a platinum dish until the temperature rises to 150°. On cooling the syrupy liquid, hard rhombic crystals of **orthophosphoric acid,** H_3PO_4, are slowly deposited. If the phosphorus used contains arsenic, the solution of phosphoric acid is treated with sulphur dioxide to reduce arsenic acid to arsenious acid, the excess of sulphur dioxide is expelled by boiling, and the arsenic precipitated as sulphide by H_2S. The filtered solution is evaporated. If yellow phosphorus is used, nitric acid of sp. gr. 1·2 is employed, to avoid explosions, and a trace of iodine may be added as a catalyst. If the temperature is carried beyond 150° in the evaporation, some metaphosphoric acid is formed, which retards crystallisation.

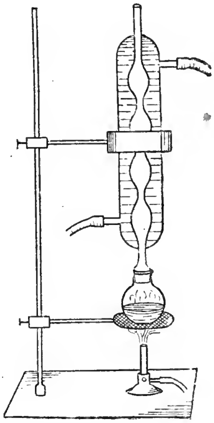


FIG. 321.—Preparation of Phosphoric Acid from Phosphorus.

The crystals of orthophosphoric acid melt at 38·6°, and are very soluble in water. Two crystalline hydrates, $2H_3PO_4,H_2O$ and $10H_3PO_4,H_2O$, are known. The aqueous solution has a strong, purely acid, taste and no smell, and has been used for making "lemonade."

The orthophosphates.—Orthophosphoric acid is **tribasic**, and forms three series of salts :

Primary orthophosphates, *e.g.*, sodium dihydrogen phosphate, NaH_2PO_4.
Secondary orthophosphates, *e.g.*, disodium hydrogen phosphate, Na_2HPO_4.
Tertiary orthophosphates, *e.g.*, trisodium phosphate, Na_3PO_4.

*Ortho*phosphates are usually called simply "phosphates." Ordinary sodium phosphate is the secondary salt, $Na_2HPO_4,12H_2O$.

The **alkali phosphates** (except lithium phosphate, Li_3PO_4) are soluble in water. The tertiary phosphates of the remaining metals are insoluble in water, but dissolve in dilute mineral acids: $Ca_3(PO_4)_2 + 6HCl \rightleftharpoons 3CaCl_2 + 2H_3PO_4$. If the acid solutions are neutralised, the phosphates are reprecipitated :

$$3CaCl_2 + 2H_3PO_4 + 6NaOH = Ca_3(PO_4)_2 + 6NaCl + 6H_2O.$$

Aluminium and ferric phosphates are insoluble, chromium phosphate is sparingly soluble, and the remaining phosphates are soluble, in acetic acid. If to a solution of a phosphate in acetic acid ferric chloride is added, the phosphoric acid is therefore precipitated as ferric phosphate, and is removed from the solution :

$$3Ca(C_2H_3O_2)_2 + 2H_3PO_4 + 2FeCl_3 = \\ 2FePO_4\ (pp.) + 3CaCl_2 + 6C_2H_4O_2.$$

An excess of ferric chloride then forms a blood-red solution of ferric acetate, $Fe(C_2H_3O_2)_3$, but on boiling the whole of the iron is precipitated as basic ferric acetate; the filtrate contains the other metals (except Al and Cr).

In qualitative analysis, if a solution contains phosphoric acid, this must be removed before adding ammonia to precipitate Group III (Fe, Al, Cr) ; otherwise the phosphates of the remaining groups (except the alkali-metals) would also be precipitated. The solution from the sulphuretted hydrogen precipitation is boiled with nitric acid to oxidise ferrous salts, nearly neutralised with sodium carbonate, and then a mixture of sodium acetate and acetic acid added. $AlPO_4$, $FePO_4$, and $CrPO_4$ are precipitated. The filtrate is then treated with ferric chloride until the deep red colour of ferric acetate appears. It is boiled, and the filtrate is free from phosphates.

The primary soluble phosphates in solution are acid to litmus ;

tertiary phosphates are alkaline ; whilst secondary phosphates are faintly alkaline—practically neutral :

$$\begin{aligned} &H_2PO_4'' && \rightleftharpoons HPO_4'' + H^{\cdot}. \\ &PO_4''' + H_2O && \rightleftharpoons HPO_4'' + OH'. \\ &(HPO_4'' + H^{\cdot} + OH' && \leftrightharpoons H_2PO_4' + OH'.) \end{aligned}$$

The first two hydrogen atoms of orthophosphoric acid are easily ionised in solution : the third is split off only with difficulty, and in presence of an excess of base :

$$H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4' \rightleftharpoons 2H^{\cdot} + HPO_4'' \leftrightharpoons 3H^{\cdot} + PO_4'''.$$

On titration with litmus, phosphoric acid therefore behaves as a dibasic acid. Methyl-orange, however, changes colour at the stage NaH_2PO_4 ; phenolphthalein at the stage Na_2HPO_4 ; the changes occur sharply at 55°.

Solutions of phosphates, when treated with excess of nitric acid and a solution of ammonium molybdate (p. 957), slowly deposit *in the cold* a canary-yellow precipitate of **ammonium phosphomolybdate,** readily soluble in ammonia.

Pyro- and meta-phosphates also give this reaction ; they are first of all converted by the reagent into orthophosphoric acid. Arsenic acid, H_3AsO_4, gives a similar precipitate, but *only on heating.* The precipitation of phosphoric acid also occurs much more rapidly on heating.

Ordinary **sodium phosphate,** $Na_2HPO_4,12H_2O$, is prepared by neutralising phosphoric acid with caustic soda or sodium carbonate (the end-point should be faintly alkaline), and evaporating. It forms efflorescent crystals, m.-pt. 35°, readily soluble in water.

If a solution of phosphoric acid is divided into three parts, the equivalent quantities of caustic soda and ammonia, respectively, added to two to form Na_3PO_4 and $(NH_4)_3PO_4$, and all three solutions mixed and evaporated, crystals of **microcosmic salt,** or sodium ammonium hydrogen phosphate, $NaNH_4HPO_4,4H_2O$, are formed. This salt may also be prepared by dissolving 6 gm. of ammonium chloride and 36 gm. of ordinary sodium phosphate in a little hot water, filtering off the sodium chloride, and crystallising.

The **primary,** or **acid sodium phosphate,** NaH_2PO_4,H_2O, is prepared by adding phosphoric acid to a solution of the ordinary phosphate, until the solution no longer precipitates barium chloride, and evaporating ; it is dimorphous. **Trisodium phosphate** is prepared by dissolving the calculated amounts of sodium phosphate and caustic soda in hot water, and evaporating ; crystals of $Na_3PO_4,12H_2O$ separate. These are not efflorescent or deliquescent. This salt is used, under the name of "tripsa," for softening boiler-water. The calcium bicarbonate is precipitated as carbonate by the alkali formed by hydrolysis, and calcium and magnesium chlorides and sulphates are precipitated as phosphates.

Pyrophosphoric acid, $H_4P_2O_7$.—This acid is formed (with a little metaphosphoric acid) when orthophosphoric acid is heated to 213°; condensation occurs, and a molecule of water is eliminated from 2 molecules of orthophosphoric acid: $2H_3PO_4 = H_4P_2O_7 + H_2O$. If ordinary sodium phosphate is heated to dull redness, it also loses a molecule of water and forms **sodium pyrophosphate** (Clark, 1827): $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$. Whereas the orthophosphate gives a *yellow* precipitate of **silver orthophosphate,** Ag_3PO_4, with silver nitrate, the residue after ignition, when dissolved in water, gives with that reagent a *white* crystalline precipitate of **silver pyrophosphate,** $Ag_4P_2O_7$. If lead nitrate solution is added to a solution of sodium pyrophosphate, a white precipitate of **lead pyrophosphate,** $Pb_2P_2O_7$, is thrown down: this, when suspended in water and treated with sulphuretted hydrogen, gives a black precipitate of lead sulphide, and a solution of **pyrophosphoric acid**:

$$Pb_2P_2O_7 + 2H_2S = 2PbS + H_4P_2O_7.$$

The solution may be evaporated *in vacuo,* and on cooling to − 10° for some time yields white granular crystals of pure **pyrophosphoric acid,** $H_4P_2O_7$, m.-pt. 61°.

If a solution of orthophosphoric acid or an orthophosphate, mixed with ammonium chloride, is made alkaline with ammonia, and a solution of a magnesium salt ($MgCl_2$ or $MgSO_4$) added, a white crystalline precipitate of **magnesium ammonium phosphate,** $MgNH_4PO_4,6H_2O$, is formed. In dilute solutions, this is deposited slowly; the precipitation is accelerated by adding excess of ammonia and scratching the sides of the beaker with a glass rod. When heated to redness, the precipitate loses ammonia and water and forms a white insoluble powder of **magnesium pyrophosphate:** $Mg_2P_2O_7$. These reactions are utilised in the detection and estimation of orthophosphoric acid or magnesium. With manganese salts, $MnNH_4PO_4,6H_2O$ and $Mn_2P_2O_7$ are formed.

If a solution of pyrophosphoric acid is kept for some time, or is boiled, orthophosphoric acid is formed: $H_4P_2O_7 + H_2O = 2H_3PO_4$. The salts, however, are very stable in solution.

Pyrophosphoric acid contains four hydrogen atoms, and is tetrabasic. Only two series of salts are, however, known, viz., the **normal salts,** $M_4P_2O_7$, and the **diacid salts,** $M_2H_2P_2O_7$. Examples are: $Na_4P_2O_7,10H_2O$ (monoclinic); $Na_2H_2P_2O_7,6H_2O$ (hexagonal); $Ca_2P_2O_7,4H_2O$ (amorphous, insoluble); $Ag_2H_2P_2O_7$ (soluble). Complex ions containing metals (Zn, Pb, Ag, etc.) are formed by dissolving the insoluble pyrophosphates in sodium pyrophosphate solution.

Metaphosphoric acid, HPO_3.—This acid is formed as a glassy residue when either ortho- or pyro-phosphoric acid is heated to redness: $H_3PO_4 = HPO_3 + H_2O$ (Graham, 1833). By prolonged heating, some phosphoric anhydride appears to be produced, and the hard glass formed on cooling crackles when thrown into water (Berzelius). The water content of the residue depends on the duration of heating; pyrophosphoric acid is formed as an intermediate product. At a white heat, the acid volatilises. If the glass is dissolved in water, the freezing-point depression shows that the acid is polymerised, $(HPO_3)_n$, whereas the solution of the acid prepared from the insoluble lead salt and hydrogen sulphide (*cf.* pyrophosphoric acid) has the simple molecular weight, HPO_3.

Sodium metaphosphate is formed as a clear glass when microcosmic salt, acid sodium orthophosphate, or acid sodium pyrophosphate is heated to redness: $NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O$; $NaH_2PO_4 = NaPO_3 + H_2O$.

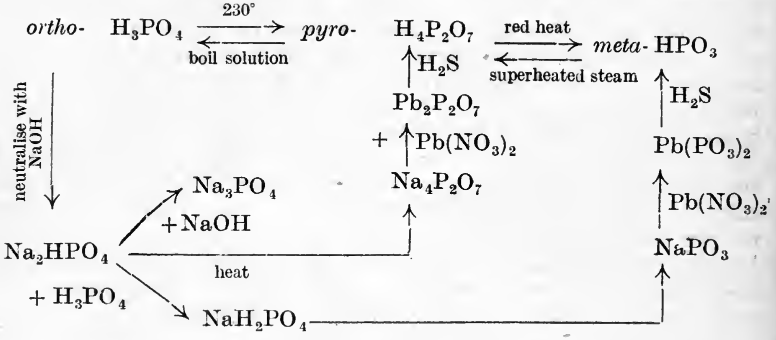
If a little microcosmic salt is heated on a loop of platinum wire, a fused bead of $NaPO_3$ remains, which dissolves many metallic oxides with the formation of orthophosphates possessing characteristic colours ("microcosmic bead"): $CoO + NaPO_3 = CoNaPO_4$ (blue).

A nearly neutralised solution of a metaphosphate gives a white *gelatinous* precipitate of **silver metaphosphate,** $AgPO_3$, with silver nitrate.

Metaphosphoric acid glass, in solution, appears to have a high molecular weight, $(HPO_3)_n$, and behaves in many ways as a **colloid.** Unlike the other phosphoric acids, it at once coagulates albumin (white of egg), and gives white precipitates with calcium and barium chlorides.

The **metaphosphates** are much more numerous than the simple formula of the acid HPO_3 would indicate, and both polymeric and metameric varieties (p. 496) appear to exist. They were investigated by Fleitmann and Henneberg (1848), who regarded them as derived from polymerised acids, $(HPO_3)_n$, where $n = 1, 2, 3, 4, 5$, and 6. Later investigations of Tammann (1890) showed that metamerism was also exhibited. A table of these compounds is given in Abegg's "Handbuch," vol. III., [3], p. 448. Sodium metaphosphate prepared from microcosmic salt appears to be $(NaPO_3)_3$; its solution is unstable. Holt and Myers (1911), by the freezing-point method, differentiated four varieties of metaphosphoric acid: (1) HPO_3, from the lead salt and H_2S; (2) the "crackling" acid; (3) the non-deliquescent glass prepared by heating (2) to redness for twenty-four hours, $(HPO_3)_2$; (4) the deliquescent glass obtained by heating the commercial acid for a short time, $(HPO_3)_3$.

The relations between the different phosphoric acids is summarised in the following diagram :



If phosphorus pentoxide is added to 30 per cent. hydrogen peroxide, cooled in ice, **monoperphosphoric acid,** H_3PO_5, or $PO(OH)_2{\cdot}O{\cdot}OH$, analogous to Caro's acid (p. 520), is formed. Pyrophosphoric acid gives a small quantity of a crystalline **perphosphoric acid,** $H_4P_2O_8$, analogous to $H_2S_2O_8$.

Basicity of acids.—Until Graham's researches (1833), the three varieties of phosphoric acid were regarded as *isomeric*, and, since they were considered to enter into the salts as anhydrous oxides, were formulated as *a* P_2O_5, *b* P_2O_5, and *c* P_2O_5. Graham found that the phosphates, with the exception of the metaphosphates, tertiary sodium phosphate, and sodium pyrophosphate, contain hydrogen, which he regarded as present in the form of combined water. He therefore supposed that the free acids are also compounds of the anhydride with varying definite proportions of water : *meta-* P_2O_5,H_2O ; *pyro-* $P_2O_5,2H_2O$; *ortho-* $P_2O_5,3H_2O$. Liebig (1838) then pointed out that the facts could be even more simply explained on Davy's **hydrogen theory of acids,** but it was then necessary to assume that the hydrogen in orthophosphoric acid, for instance, could be replaced in three stages, or, as Liebig expressed it, this compound is a **tribasic acid :**

	Graham.	Liebig.
Orthophosphoric acid	$P_2O_5,3H_2O$	H_3PO_4
Acid sodium phosphate	$P_2O_5,Na_2O,2H_2O$	H_2NaPO_4
Ordinary sodium phosphate ...	$P_2O_5,2Na_2O,H_2O$	HNa_2PO_4
Trisodium phosphate	$P_2O_5,3Na_2O$	Na_3PO_4

Phosphorus oxychloride, $POCl_3$.—When phosphorus pentachloride is treated with small quantities of water until the solid is completely liquefied, a colourless fuming liquid, b.-pt. 107°, m.-pt.

— 1·5°, is formed which has the composition $POCl_3$ and is known as **phosphorus oxychloride**: $PCl_5 + H_2O = POCl_3 + 2HCl$. It is also formed by the direct oxidation of phosphorus trichloride by ozone, or by the gradual addition of 32 gm. of powdered potassium chlorate to 100 gm. of phosphorus trichloride, and then distilling: $3PCl_3 + KClO_3 = 3POCl_3 + KCl$. Phosphorus pentachloride and pentoxide combine to form the oxychloride when heated in a sealed tube: $P_2O_5 + 3PCl_5 = 5POCl_3$.

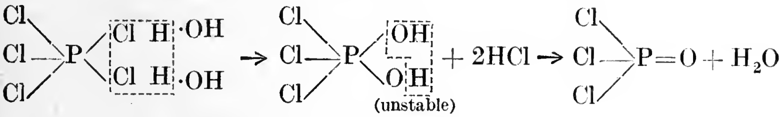
The formation of the oxychloride by the action of phosphorus pentachloride on compounds containing hydroxyl groups has already been described (p. 624); the action on oxalic and boric acids is interesting in this connection, since, in the first case, the by-products are gaseous, and are evolved, leaving the phosphorus oxychloride, and, in the second case, the by-product is non-volatile, so that the oxychloride may be distilled off:

$$\begin{aligned} C_2O_4H_2 + PCl_5 &= POCl_3 + CO_2 + CO + 2HCl. \\ 2H_3BO_3 + 3PCl_5 &= B_2O_3 + 3POCl_3 + 6HCl. \end{aligned}$$

The oxychloride is readily hydrolysed by excess of water, forming orthophosphoric acid: $POCl_3 + 3H_2O = H_3PO_4 + 3HCl$.

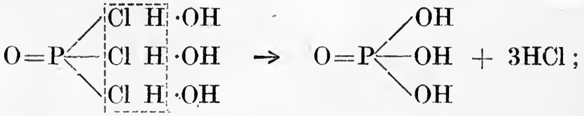
Phosphorus oxybromide, $POBr_3$ (solid; b.-pt. 190°), is similarly prepared from the pentabromide: the **oxyfluoride,** POF_3 (b.-pt. — 40°), is formed by the action of dry HF on P_2O_5, by the action of zinc fluoride on $POCl_3$, or by the explosion of PF_3 and oxygen by a powerful induction spark; it does not attack glass.

Constitution of phosphoric acids.—From its method of preparation, phosphorus oxychloride is ascribed the formula $O = P(Cl_3)$:



It contains the tervalent radical **phosphoryl,** $\mathrm{O{:}P}\begin{smallmatrix}/\\—\\\backslash\end{smallmatrix}$. It is more stable than the pentachloride, which may be regarded as containing the radical $\mathrm{Cl_2{:}P}\begin{smallmatrix}/\\—\\\backslash\end{smallmatrix}$, since the pentachloride is decomposed on heating, whilst the oxychloride volatilises unchanged.

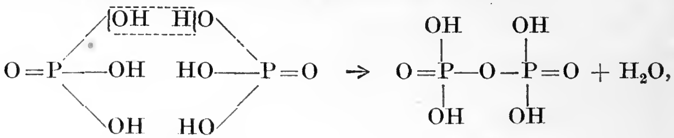
Since orthophosphoric acid is produced by the action of water on phosphorus oxychloride (or **phosphoryl chloride,** as it may be called), the latter may be regarded as the **chloride of orthophosphoric acid,** just as sulphuryl chloride is the chloride of sulphuric acid (p. 514). Phosphorus pentachloride is the chloride of a hypothetical acid, $P(OH)_5$, which, if it existed, would be the *true ortho*phosphoric acid. Orthophosphoric acid, therefore, contains the radical phosphoryl :

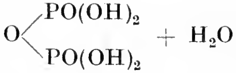


its formula may be written $O:P(OH)_3$. The fact that the third atom of hydrogen is only removed with difficulty by bases is no proof that all three hydroxyl groups cannot be similarly attached to the phosphorus atom, since sulphuric acid, which is always written $SO_2(OH)_2$, is only slightly ionised in the second stage, except at very great dilutions. In reactions where ions are not concerned, all three hydroxyl groups of orthophosphoric acid may be readily removed, as in the formation of the ethyl ester, $O:P(OC_2H_5)_3$.

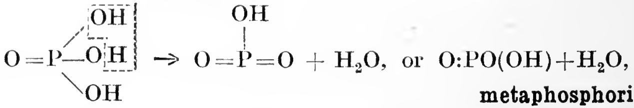
Although the two possible isomers of phosphorus oxychloride, $O=\overset{V}{P}Cl_3$ and $ClO-\overset{III}{P}Cl_2$, are not known, the corresponding phenyl compounds, $O:P(C_6H_5)_3$ (m.-pt. 153·5°), and $C_6H_5O\cdot P(C_6H_5)_2$ (b.-pt. 265°/62 mm.), have been prepared.

From the formula $O:P(OH)_3$ for orthophosphoric acid, those of pyrophosphoric and metaphosphoric acids, and (though with less probability) that of phosphoric anhydride may be inferred :

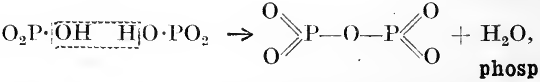
(1) 

or 

pyrophosphoric acid.

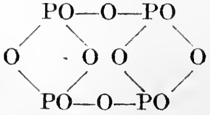
(2) 

metaphosphoric acid.

(3) 

phosphorus pentoxide.

Another suggested formula for the anhydride, which is derived from that of pyrophosphoric acid by repeated elimination of water, is :



This corresponds with the molecular formula P_4O_{10}.

The chloride of pyrophosphoric acid, **pyrophosphoryl chloride,** $P_2O_3Cl_4$, or  $O\begin{matrix}\diagup POCl_2\\ \diagdown POCl_2\end{matrix}$, is formed by oxidising phosphorus trichloride at a low temperature with nitrogen tetroxide, N_2O_4, and distilling. Nitrosyl chloride, phosphorus pentoxide, and phosphoryl chloride are also formed in this reaction. Pyrophosphoryl chloride is a colourless fuming liquid, b.-pt. 210–215°, hydrolysed by water to *ortho*phosphoric acid: $P_2O_3Cl_4 + 5H_2O = 2H_3PO_4 + 4HCl$. By distillation under reduced pressure, it gives **metaphosphoryl chloride,** PO_2Cl, a syrupy liquid.

Thiophosphoric acids.—The compounds (*cf.* thiosulphuric acid, p. 520) **monothiophosphoric acid,** $H_3P(SO_3)$; **dithiophosphoric acid,** $H_3P(S_2O_2)$; and **trithiophosphoric acid,** $H_3P(S_3O)$, are formed as sodium salts by adding phosphorus pentasulphide to caustic soda, and precipitating by alcohol. At 20° the trithiophosphate, at 50° the dithiophosphate, $Na_3PS_2O_2,11H_2O$, and at 90° the monothiophosphate, $Na_3PSO_3,12H_2O$, are formed. These precipitate barium; barium and strontium; and calcium, barium, and strontium salts, respectively. **Thiophosphoryl chloride,** $PSCl_3$, is a colourless fuming liquid, b.-pt. 125°, obtained by heating P_2S_5 and PCl_5: $P_2S_5 + 3PCl_5 = 5PSCl_3$. It is hydrolysed by water: $PSCl_3 + 4H_2O = H_2S + 3HCl + H_3PO_4$.

Magnesium ammonium thiophosphates are sparingly soluble in dilute ammonia. Dithiophosphates give a green colour with manganese and cobalt salts; cobalt monothiophosphate is intensely blue, and the nickel salt bright green.

Phosphorus trioxide, P_4O_6.—The formation of a lower oxide of phosphorus, usually assumed to be P_2O_3, by the slow oxidation of phosphorus in air, or its combustion in a limited supply of air (p. 626), was noticed by Sage (1777), but the substance was first obtained in a pure state by Thorpe and Tutton in 1890. Phosphorus is burnt in a limited supply of air, and the product condensed by cooling.

Sticks of phosphorus $1\frac{1}{2}$ in. long were placed in the hard glass tube, *a*, (Fig. 322), connected with the Liebig's condenser, *b*, 2 ft. in length, the inner tube of which was one inch in diameter. A plug of glass wool in this at the end furthest from the phosphorus served to filter out the solid pentoxide formed, whilst the trioxide was kept in the state of vapour by circulating water at 60° in the condenser. The condenser communicated with a U–tube, *c*, having a small bottle at the lower part, which was immersed in pounded ice, and this was connected through a wash-bottle, *f*, containing sulphuric acid with a water-pump for aspirating air through the apparatus. The phosphorus was ignited, and a slow current of air drawn through. The reaction was stopped when four-fifths of the phosphorus was burnt. The trioxide condensed in the U–tube; on warming the latter, it collected as a liquid in the bottle.

The trioxide is also formed by the action of phosphorus trichloride on phosphorous acid.

Phosphorus trioxide is a white, waxy, crystalline solid, m.-pt. 22·5°, b.-pt. 173·1°. The vapour density and the depression of freezing point of benzene correspond with the formula P_4O_6 (*cf.* As_4O_6, Sb_4O_6). Unless quite pure, the trioxide slowly turns red in sunlight from separation of phosphorus. It is very poisonous, and has an unpleasant odour of garlic. Phosphorus trioxide oxidises in air or oxygen at the ordinary temperature, forming the pentoxide; at 70° it inflames in air. Under reduced pressure it glows in air, ionising it, but not forming any ozone (*cf.* phosphorus vapour). If heated in oxygen it burns; in chlorine it inflames spontaneously, forming $POCl_3$, and the chloride of metaphosphorous acid, PO_2Cl, or possibly a mixture of $P_2O_3Cl_4$ (p. 637) and $P_7O_{15}Cl_5$. In cold water, phosphorus trioxide dissolves *slowly* (*cf.* P_2O_5), forming **phosphorous acid**, H_3PO_3, of which it is the anhydride. Hot water brings about explosive decomposition, with formation of phosphine, red phosphorus, and phosphoric acid:

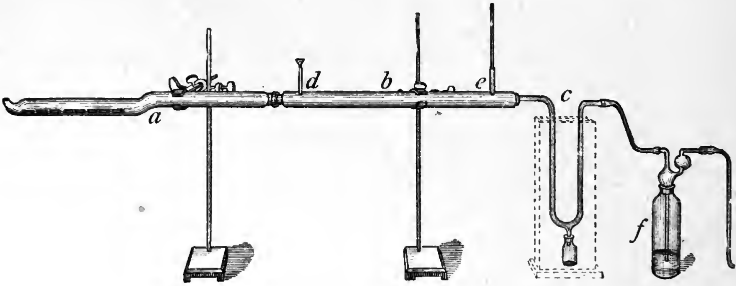


FIG. 322.—Preparation of Phosphorus Trioxide.

$$P_4O_6 + 6H_2O = PH_3 + 3H_3PO_4.$$

Alkalies act similarly. Phosphorus trioxide (or **phosphorous anhydride**) ignites in contact with absolute alcohol: ether, carbon disulphide, benzene, and chloroform dissolve it without decomposition. With ammonia, it forms the diamide of phosphorous acid, $HO{\cdot}P(NH_2)_2$.

Phosphorus tetroxide, P_2O_4.—When liquid P_4O_6 is heated in a sealed tube it is stable up to 200°; at 210° it becomes turbid, and at 290° a sublimate of **phosphorus tetroxide,** P_2O_4, and a residue of red phosphorus are formed: $2P_4O_6 = 3P_2O_4 + 2P$. The tetroxide sublimes *in vacuo* at 180°. If phosphorus is burnt in a tube in a limited supply of air, a buff-coloured powder is deposited on the cooler part, which consists of a mixture of P_4O_{10}, P_4O_6, and red phosphorus. On heating this in a sealed tube, a white crystalline sublimate of P_2O_4 is formed : $P_2O_3 + P_2O_5 = 2P_2O_4$. With water, this gives a mixture of phosphorous and phosphoric acids : $P_2O_4 + 3H_2O = H_3PO_3 + H_3PO_4$.

An oxide, P_2O, is said to be formed as a reddish-yellow powder by the action of the silent discharge on a mixture of hydrogen and $POCl_3$ vapour, by the action of PH_3 on $POBr_3$, or by heating phosphorous acid and $POCl_3$: $2H_3PO_3 = 3H_2O + P_2O_3$; $2P_2O_3 = P_2O_5 + P_2O$.

Phosphorous acid, H_3PO_3.—Phosphorous acid, H_3PO_3, is formed when the trioxide is dissolved in cold water, but is most conveniently prepared by the action of water on its acid chloride, phosphorus trichloride (Davy, 1812) : $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$.

To minimise the decomposing action of the rise of temperature produced, a stream of air may be passed through the trichloride and the vapour passed into ice-cold water. Or the trichloride may be added to concentrated hydrochloric acid, when gaseous hydrogen chloride is evolved, and the heat of reaction is then diminished by the heat absorbed in the evolution of hydrochloric acid gas from the solution. The formation and decomposition of the trichloride may be carried on simultaneously by passing chlorine through phosphorus melted under water.

The solution is evaporated until the temperature rises to 180°, hydrogen chloride being driven off, and it then crystallises on cooling. The crystalline acid is also obtained by heating PCl_3 with oxalic acid until frothing ceases, and then cooling :

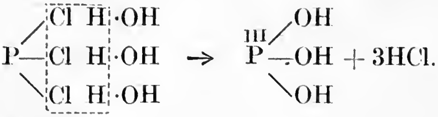
$$PCl_3 + 3C_2H_2O_4 = H_3PO_3 + 3CO_2 + 3CO + 3HCl.$$

Phosphorous acid forms white crystals, m.-pt. 71·7° ; it is very soluble in water. When heated it decomposes, evolving pure phosphine, and leaving metaphosphoric acid : $4H_3PO_3 = 3HPO_3 + 3H_2O + PH_3$. If the acid is heated in the air, the phosphine ignites and burns in bright flashes. This result is obtained by heating the residue obtained by burning phosphorus in a confined volume of air over water ; this contains phosphorous acid, formed from phosphorus trioxide. Phosphorous acid is a **powerful reducing agent,** precipitating many metals, such as gold, from solutions of their salts, and it reduces mercuric to mercurous chloride :

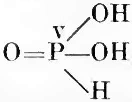
$$2HgCl_2 + H_2O + H_3PO_3 = Hg_2Cl_2 \text{ (pp.)} + 2HCl + H_3PO_4.$$

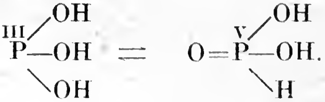
Silver nitrate gives first a white precipitate of phosphite, Ag_3PO_3, which rapidly turns black from formation of metallic silver. Phosphorous acid precipitates sulphur from a solution of sulphurous acid : $H_2SO_3 + 2H_3PO_3 = 2H_3PO_4 + H_2O + S$; it is slowly oxidised by solutions of iodine and potassium permanganate.

Wurtz found that phosphorous acid, although it has the formula H_3PO_3, is **dibasic;** only two atoms of hydrogen can be replaced by metals to form salts. Its preparation from phosphorus trichloride points to the formula $P(OH)_3$:

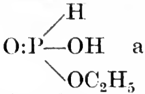
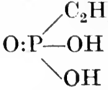


$$\mathrm{P}\begin{array}{l}\diagup \boxed{\begin{array}{l}\mathrm{Cl\ H}\\ \mathrm{Cl\ H}\\ \mathrm{Cl\ H}\end{array}}\begin{array}{l}\cdot\mathrm{OH}\\ \cdot\mathrm{OH}\\ \cdot\mathrm{OH}\end{array}\\ \end{array} \rightarrow \overset{\mathrm{III}}{\mathrm{P}}\begin{array}{l}\diagup\mathrm{OH}\\ —\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array} + 3\mathrm{HCl}.$$

To explain its dibasic character, however, the formula of the acid is usually written:  $\mathrm{O{=}\overset{V}{P}}\begin{array}{l}\diagup\mathrm{OH}\\ —\mathrm{OH}\\ \diagdown\mathrm{H}\end{array}$, the hydroxyl hydrogen atoms being ionised in solution, whilst the hydrogen atom directly attached to the phosphorus (which is quinquevalent) is not split off as an ion (*cf.* p. 517). It is supposed that, although the formula may be $P(OH)_3$ at the instant of its formation from the trichloride, the molecule of the acid undergoes almost immediate internal rearrangement, or **tautomeric change** (p. 497):



$$\overset{\mathrm{III}}{\mathrm{P}}\begin{array}{l}\diagup\mathrm{OH}\\ —\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array} \rightleftharpoons \mathrm{O{=}\overset{V}{P}}\begin{array}{l}\diagup\mathrm{OH}\\ —\mathrm{OH}.\\ \diagdown\mathrm{H}\end{array}$$

The existence of two isomeric ethyl phosphorous acids, which may be written  $\mathrm{O{:}P}\begin{array}{l}\diagup\mathrm{H}\\ —\mathrm{OH}\\ \diagdown\mathrm{OC_2H_5}\end{array}$ and  $\mathrm{O{:}P}\begin{array}{l}\diagup\mathrm{C_2H_5}\\ —\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array}$, supports this hypothesis. Normal esters of phosphorous acid, *e.g.*, **ethyl phosphite,** $P(OC_2H_5)_3$, are, however, also known, and the dibasic character of the acid may simply be due to the increasing difficulty of splitting off hydrogen ions in the successive dissociations: $H_3PO_3 \rightleftharpoons H^{\cdot} + H_2PO_3{}' \rightleftharpoons H^{\cdot} + H^{\cdot} + HPO_3{}'' \rightleftharpoons 3H^{\cdot} + PO_3{}'''$. The reducing properties of the acid, however, appear to be due to the hydrogen atom directly attached to phosphorus.

The two series of salts known are RH_2PO_3 and R_2HPO_3. When boiled with alkalies, they evolve hydrogen: $H_3PO_3 + 3KOH = K_3PO_4 + 2H_2O + H_2$.

The acid H_3PO_3 is **orthophosphorous acid. Pyrophosphorous acid,** $H_4P_2O_5$, or, since it is dibasic, $H_2(H_2P_2O_5)$, is formed by shaking PCl_3 with H_3PO_3 for five hours at 30–40°, and leaving in a desiccator over P_2O_5; it forms needles, m.-pt. 38°. **Metaphosphorous acid,** HPO_2, is formed in crystals by the oxidation of phosphine by oxygen under 25 mm. pressure: $PH_3 + O_2 = HPO_2 + H_2$. When phosphine is exploded with oxygen, this reaction occurs, together with the reaction $2PH_3 + 3O_2 = 2H_3PO_3$.

Phosphorous acid reacts with phosphorus pentachloride in the normal manner, forming the acid chloride, PCl_3:$H_3PO_3 + 3PCl_5 = PCl_3 + 3POCl_3 + 3HCl$.

Hypophosphoric acid, H_2PO_3.—If sticks of phosphorus, enclosed in glass tubes open at both ends (Fig. 323), are supported in a glass funnel over a beaker of water under a bell-jar, oxidation occurs, with the production of fumes, which sink into the beaker and dissolve, rendering the water acid. Dulong first noticed that the acid made in this way, called "Pelletier's phosphorous acid" (1796), differed from ordinary phosphorous acid; he called it **phosphatic acid.** Salzer (1877) found that if the liquid is partially neutralised with caustic soda, sparingly soluble crystals of the composition $NaHPO_3,3H_2O$ slowly separate from the acid liquid. If lead nitrate is added to a solution of this salt, the lead compound, $PbPO_3$, is precipitated; on suspending this in water and passing sulphuretted hydrogen, a solution of the free acid, now usually called **hypophosphoric acid,** H_2PO_3, is obtained. This on evaporation in a vacuum desiccator over sulphuric acid gives crystals, H_2PO_3,H_2O, which readily lose water and give H_2PO_3.

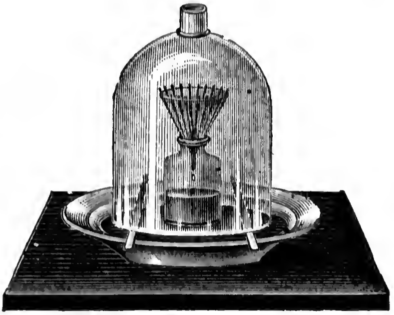
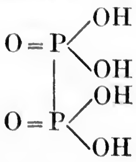


FIG. 323.—Preparation of Hypophosphoric Acid.

If phosphorus is heated on a water-bath with a solution of copper nitrate, or an acid solution of silver nitrate, copper or silver phosphides, and then salts of hypophosphoric acid, are formed. Six gm. of silver may be dissolved in 100 gm. of nitric acid diluted with its own volume of water, and 9 gm. of white phosphorus added. When the violent reaction which occurs on heating subsides, the solution is cooled, and silver hypophosphate, Ag_2PO_3, separates; this may be decomposed by hydrochloric acid to obtain hypophosphoric acid.

Hypophosphoric acid on heating decomposes with evolution of phosphine, leaving phosphoric acid. It differs from phosphorous acid in having no reducing action on metallic salts. The hypophosphates are oxidised by bromine water to pyrophosphates, which indicates that the formula of the acid is:



The simpler formula, $H_2\overset{\text{IV}}{P}O_3$, is now adopted, since the vapour density of the ester shows that it has the formula $(C_2H_5)_2PO_3$. The existence of an acid salt, $Na_3HP_2O_6,9H_2O$, may be cited in evidence of the formula $H_4P_2O_6$, although this salt may be $3Na_2PO_3 + H_2PO_3 + 18H_2O$. Hypophosphoric acid is rapidly oxidised by potassium permanganate, but phosphorus tetroxide, P_2O_4, is only slowly oxidised. This oxide, with water, produces only a mixture of phosphoric and phosphorous acids : it is probably not the true anhydride of hypophosphoric acid, but is **phosphoryl phosphate,**

$O{:}P{\cdot}O{\cdot}P\begin{matrix}\diagup O\\ \diagdown O\end{matrix}$.

Hypophosphorous acid, H_3PO_2.—This acid was discovered by Dulong in 1816. The residue from the preparation of phosphine from phosphorus and alkali (p. 618) contains a salt of **hypophosphorous acid,** H_3PO_2. The acid is prepared by warming white phosphorus with baryta water :

$$2P_4 + 3Ba(OH)_2 + 6H_2O = 2PH_3 + 3Ba(H_2PO_2)_2.$$

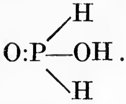
The solution is filtered from barium phosphate also formed, the excess of baryta is removed by carbon dioxide, and the barium hypophosphite, $Ba(H_2PO_2)_2,H_2O$, recrystallised. A solution of barium hypophosphite is then decomposed with the calculated amount of sulphuric acid :

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2.$$

The filtrate is carefully evaporated, below 130°, to a syrup, cooled to 0° in a desiccator over P_2O_5 and KOH, and crystallised. The acid is also formed by passing carbon dioxide saturated with the vapour of phosphorus trichloride into a paste of water and phosphorus trioxide.

Hypophosphorous acid melts at 17·4°; on heating it decomposes at 130°, becoming yellow, and evolving phosphine : $4H_3PO_2 = 2HPO_3 + 2PH_3 + 2H_2O$. The salts also evolve phosphine on heating :

$$4NaH_2PO_2 = 2PH_3 + 2Na_2HPO_4 = 2PH_3 + Na_4P_2O_7 + H_2O.$$

Hypophosphorous acid and its salts are **powerful reducing agents,** precipitating metals from solutions of their salts. Thus, silver nitrate gives a black precipitate of silver. From copper salts, cuprous hydride, CuH, is thrown down, which evolves hydrogen on warming with hydrochloric acid. The acid is **monobasic,** forming crystalline salts such as **sodium hypophosphite,** NaH_2PO_2,H_2O, and **calcium hypophosphite,** $Ca(H_2PO_2)_2$. These are prepared by boiling phosphorus with caustic soda, or milk of lime, respectively, and are used medicinally as tonics. Since it is monobasic, the acid is usually given the formula 

$$O{:}P\begin{matrix}\diagup H\\ -OH\\ \diagdown H\end{matrix}$$

.

The hydrogen atoms directly attached to phosphorus have reducing properties (*cf.* phosphorous acid). All hypophosphites are soluble in water. The acid is reduced by zinc and hydrochloric acid to phosphine.

EXERCISES ON CHAPTER XXXI

1. Give a general account of the properties of the elements of the nitrogen group, with special reference to the change of properties with increase of atomic weight.

2. What are the chief minerals containing phosphorus ? How is the element prepared on the large scale ? How is it purified, and for what purposes is it used ?

3. Discuss the valency of phosphorus in its compounds. It was once assumed that PCl_5 was a "molecular compound," $\overset{\text{III}}{P}Cl_3,Cl_2$. What facts make this improbable ?

4. What happens when (*a*) phosphorus is boiled with caustic soda solution, (*b*) phosphorous acid is heated, (*c*) chlorine is passed through phosphorus fused under water, (*d*) silver nitrate is added to a solution of ordinary sodium phosphate ? Give equations.

5. Describe the allotropic modifications of phosphorus. How may red phosphorus be obtained from yellow phosphorus, and *vice versa* ?

6. Describe briefly the preparation and properties of the hydrogen compounds of phosphorus. Compare their properties with those of nitrogen.

7. What is the action of water on (*a*) calcium phosphide, (*b*) phosphorus trichloride, (*c*) phosphorus tri-iodide, (*d*) phosphorus pentachloride, (*e*) metaphosphoric acid ?

8. Tabulate the properties and reactions of: (1) yellow and red phosphorus ; (2) ortho-, pyro-, and meta-phosphoric acids, so as to show their differences.

9. You are given a solution which may contain a phosphite, a hypophosphite, or a hypophosphate. Explain carefully, giving equations, how you would distinguish between salts of these acids.

10. How are the lower oxides of phosphorus prepared ? What is the action of water upon them ?

11. Describe the preparation and properties of the sulphides of phosphorus, and thiophosphoryl chloride.

CHAPTER XXXII

ARSENIC AND ITS COMPOUNDS

Arsenic.—The two minerals *realgar* (red), As_2S_2, and *orpiment* (yellow), As_2S_3, were known to the ancients, but were confused with cinnabar (HgS), under the name *sandarach*, or *arsenicon*. The Greek alchemist Olympiodorus (fifth century) describes the production of *white arsenic* (arsenious oxide, As_4O_6) by roasting the sulphides in air; he calls it "white alum." The element arsenic itself, obtained as a sublimate, was also known, and used for whitening copper, forming an alloy with the metal, and was thence regarded as a "second mercury." Arsenical compounds, which are very poisonous, were introduced into medicine by Paracelsus in the sixteenth century (*cf.* p. 29). The composition of white arsenic, as the calx of "metallic" arsenic, was recognised by Brandt in 1773.

The chief **minerals** containing arsenic are the sulphides, *orpiment* (As_2S_3) and *realgar* (As_2S_2); the oxide, *arsenite*, As_4O_6; *arsenical iron*, $FeAs_2$; *arsenical nickel*, NiAs; *nickel glance*, NiAsS; *tin-white cobalt*, $(Co,Ni,Fe)As_2$; *arsenical pyrites*, or *mispickel*, FeAsS; *cobaltite*, CoAsS; and certain oxidised compounds containing salts of **arsenic acid**, H_3AsO_4; *pharmacolite*, $(CaHAsO_4)_2 + 5H_2O$; *cobalt bloom*, $Co_3(AsO_4)_2 + 8H_2O$; and *mimetisite*, $2Pb_3(AsO_4)_2,Pb_2(PO_4)Cl$. The free element is also found in large quantities.

Iron pyrites and other sulphide ores often contain arsenic, which appears to replace sulphur, and function as a bivalent element: $Fe(As,S)_2$. Sulphuric acid prepared from arsenical pyrites may contain 1 per cent. of As_2O_3 (p. 508), and coal smoke, especially in yellow fogs, may contain arsenious oxide, from the pyrites in the coal. Traces of arsenic occur in nearly all materials, including the human body, and most foods. About 10,000 tons of arsenic compounds are produced annually, mostly in the Freiburg Smelteries.

Arsenious oxide, As_2O_3.—In *roasting* minerals in a current of air, for metallurgical treatment, fumes of **arsenious oxide,** As_4O_6 (or, since the molecular weight of the solid is unknown, As_2O_3), are often evolved, and may be condensed in flues as an impure powder: *e.g.*, $4CoAsS + 9O_2 = 4CoO + 4SO_2 + 2As_2O_3$. This may be obtained in larger quantities by roasting rich arsenical ores, such as mispickel.

A suitable apparatus is the **revolving calciner** of Oxland and Hocking (Fig. 324), consisting of a rotating iron cylinder lined with refractory material, down which the crushed ore slides from a hopper above. The ore is met by flames and hot gases from a furnace at the lower end. The "arsenical soot" is collected in flues, and the roasted ore, freed from arsenic, drops into a wagon for use in the smelting furnace.

The impure arsenious oxide may be purified by sublimation in iron pots, and the *white arsenic* so obtained is the source of all the arsenic compounds of commerce. The production at present exceeds the demand.

Arsenious oxide is used as a poison for vermin, in taxidermy for preserving skins, and in glass-making for removing colour from the glass. In minute amounts it is used medicinally as a tonic, and in diseases of the skin.

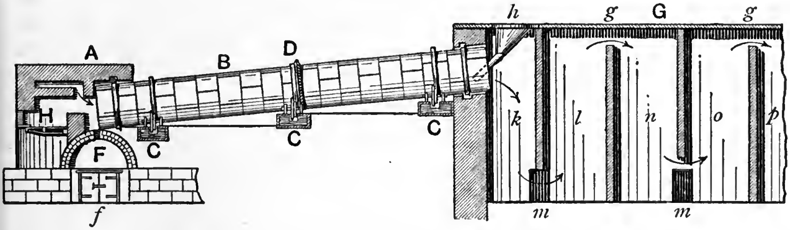


FIG. 324.—Oxland and Hocking's Revolving Calciner.

Arsenic.—The element ("metallic arsenic") occurs native, and is also obtained by heating arsenical pyrites with iron, or by reducing the trioxide with charcoal. The powdered mixture is heated in a clay crucible, covered with an inverted iron cone, into which the arsenic sublimes: $As_4O_6 + 6C = 6CO + As_4$. It is also prepared on the larger scale by heating mispickel in a clay tube, fitted for half its length with an inner tube of sheet iron. The iron tube is afterwards unrolled to split off the arsenic: $FeAsS = FeS + As$. Arsenic is purified by resublimation from charcoal powder. Arsenic sulphides are not reduced by heating with charcoal; with potassium cyanide, they give arsenic.

EXPT. 261.—Heat a little arsenious oxide with powdered charcoal and potassium cyanide in a dry test-tube. A black mirror of arsenic sublimes in the tube. If this is heated, it is oxidised, and a white sublimate of arsenious oxide forms higher up in the tube.

Allotropic forms of Arsenic.—As in the case of phosphorus (p. 614), the element exists in different **allotropic forms.**

The following modifications of arsenic have been described :

(1) α-**Arsenic,** or **yellow arsenic,** corresponding with yellow phosphorus ; soluble in carbon disulphide ; an unstable form ; sp. gr. 3·7 (Schuller, 1889).

(2) β-**Arsenic,** or **black arsenic,** sp. gr. 4·7 ; less stable than γ-arsenic ; insoluble in carbon disulphide (Retgers, 1893).

(3) γ-**Arsenic,** or **grey arsenic** ("metallic arsenic"), the stable and ordinary form, corresponding with "metallic" phosphorus ; sp. gr. 5·73 ; insoluble in carbon disulphide.

Grey arsenic forms steel-grey, brittle, hexagonal-rhombohedral crystals, with a metallic lustre, which are fairly good conductors of heat and electricity. It volatilises slowly at 100° ; at 450° it sublimes rapidly, without previous fusion, forming a lemon-yellow vapour, the density of which varies with the temperature, indicating the dissociation : $As_4 \rightleftarrows 2As_2$.

Temp.	860°	1714°	1736°
Δ (H = 1)	147	79	77

(Theoretical : As_4 150 ; As_2 75.)

In respect of its molecular weight, arsenic resembles phosphorus, and differs from the metals, which are usually monatomic. When heated in a sealed tube under pressure, grey arsenic melts at 480°.

Grey arsenic is not oxidised in dry air, but in presence of moisture it rapidly becomes covered with a blackish-grey film, containing the trioxide. When heated to 200° in air it shows a distinct phosphorescence ; at 400° it burns in air with a white flame. The element burns brilliantly in oxygen : $As_4 + 3O_2 = As_4O_6$.

EXPT. 262.—Heat 1 gm. of arsenic in a current of oxygen in a hard glass tube connected with an empty flask, the exit tube from which passes to a U-tube packed with glass wool to keep back arsenious oxide. The arsenic burns with a brilliant flame, producing white solid arsenious oxide.

Powdered arsenic takes fire in chlorine, forming the trichloride. Arsenic combines with most metals to form fusible **arsenides ;** 0·3–1 per cent. of arsenic alloyed with lead makes the latter harder and more fusible. If this alloy is allowed to flow through a sieve, the drops of fused metal, falling down a tower into water, assume a spherical shape, and form shot.

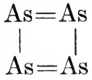
Hydrochloric acid dissolves arsenic only in the presence of air : the trioxide is probably first formed :

$$As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O.$$

Dilute nitric acid has little action in the cold ; the hot dilute acid slowly oxidises arsenic to **arsenic acid**, H_3AsO_4, and this is rapidly formed with concentrated nitric acid, or *aqua regia.* Hot concentrated sulphuric acid is reduced to sulphur dioxide, and an unstable **arsenious sulphate**, $As_2(SO_4)_3$, appears to be formed, but decomposes into the oxide. Arsenic is insoluble in alkalies.

β-Arsenic, or **black arsenic,** is formed when ordinary arsenic is rapidly heated in a glass tube in a current of hydrogen, when the element volatilises, and is deposited on the cold tube further on, partly in grey rhombohedral crystals of γ-arsenic, near the heated portion of the tube, and partly as a black, shining, *amorphous* deposit of β-arsenic in the cooler portion (210–220°). (In the cold part of the tube a *grey* crystalline deposit often appears, which may be a fourth form.) β-arsenic is not appreciably oxidised by air even at 80°. On heating to 360° it forms γ-arsenic, and may be simply a physical modification of the latter.

Yellow arsenic, or **α-arsenic**, is a peculiar allotropic form, resembling yellow phosphorus, produced by rapidly cooling arsenic vapour. Arsenic is distilled in a current of carbon dioxide, and the gases are passed into a U-tube, where they meet a current of cooled carbon dioxide. The gases are then led into cold carbon disulphide, which dissolves the α-arsenic (8 gm. in 100 c.c. at 20°). On evaporation, light yellow regular crystals are deposited, which rapidly oxidise in the air at the ordinary temperature with a faint luminescence and a garlic odour, thus behaving like yellow phosphorus. On exposure to light, even at − 180°, they rapidly pass into γ-arsenic. Yellow arsenic is also formed quantitatively by volatilising γ-arsenic *in vacuo* and cooling with liquid air. Its molecular weight in solution in carbon disulphide corresponds with As_4; the formula may be



By the action of stannous chloride on a solution of arsenious oxide a brown precipitate of arsenic is formed, part of which is soluble in carbon disulphide, and consists of α-arsenic. The proportion of the latter is increased if the mixture is shaken with carbon disulphide during the reduction, since the solution of α-arsenic is more stable than the solid.

Arsenic trihydride, AsH_3.—The only hydrogen compound of arsenic definitely known is the **trihydride**, AsH_3, called **arsine**, or **arseniuretted hydrogen**. It is a colourless gas, b.-pt. − 55°, m.-pt. − 119°. It is not formed by direct combination of the elements, but is produced by the action of *nascent* hydrogen on a soluble arsenic compound. Thus, if a solution of arsenious oxide is added to a mixture of zinc and sulphuric acid which is evolving hydrogen, or to sodium amalgam, the gas acquires a very unpleasant smell of garlic, is extremely poisonous, and burns with a green flame (Scheele, 1775). It is also formed at the cathode by the electrolysis of solutions of arsenious oxide and by boiling a soluble arsenic compound with zinc and caustic potash; antimony does *not* form a hydride in the latter reaction (Fleitmann, 1850). The gas obtained by all these processes is largely diluted with hydrogen. If it is passed through a tube cooled in liquid air, the arsine is liquefied, and on warming the pure gas is evolved.

Pure arsine may also be prepared by the action of dilute sulphuric acid on **zinc arsenide,** Zn_3As_2, prepared by heating arsenic and zinc in a crucible: $Zn_3As_2 + 6HCl = 2AsH_3 + 3ZnCl_2$; by the action of water on **sodium arsenide,** which is formed by passing the impure gas over heated sodium: $Na_3As + 3H_2O = AsH_3 + 3NaOH$; by heating sodium formate (dried at 210°) with sodium arsenite; or, most conveniently, by the action of warm water on **aluminium arsenide,** obtained by heating together aluminium powder and powdered arsenic in a covered crucible: $AlAs + 3H_2O = Al(OH)_3 + AsH_3$. The gas is exceedingly poisonous, although from the experience of the author this property seems to have been somewhat overrated. By the growth of moulds in presence of arsenic compounds (*e.g.*, Scheele's green in wall-paper), **ethyl arsine,** $AsH_2C_2H_5$, is formed; this smells of arsine, and is poisonous.

On exposure to light in the moist condition, arsine is rapidly decomposed, with deposition of a black, shining deposit of arsenic on the side of the jar; a little yellow arsenic is usually formed. The gas is decomposed by heat into its elements, the reaction commencing at about 230°: after decomposition, the volume of the gas increases in the ratio 3 : 2—$2AsH_3 = 2As + 3H_2$. From this result, and the density, the formula of the gas is found.

Arsine differs from ammonia and resembles phosphine in being almost insoluble in water. Unlike phosphine, it is almost insoluble in alcohol; it is nearly insoluble in ether, but dissolves readily in turpentine.

The Marsh-Berzelius test.—The formation of a gaseous hydride and its ready decomposition by heat form the basis of the very delicate **Marsh-Berzelius test.** Since, if a soluble arsenic compound is added to zinc and acid evolving hydrogen, the whole of the arsenic is ultimately expelled as hydride, the test may be used quantitatively.

Expt. 263.—Hydrogen is generated in a flask from pure (electrolytic) zinc and pure dilute sulphuric acid; the gas is freed from traces of sulphuretted hydrogen by a roll of dry lead acetate paper in the first part of the drying tube, the second half of which is packed with pure granular calcium chloride, separated from the paper by a plug of cotton-wool (Fig. 325). The dry gas then passes through a hard glass tube, constricted as shown, and heated at one point to dull redness by a Bunsen flame. If the materials are free from arsenic, no stain is produced in this tube beyond the heated portion. If now a few drops of a *dilute* solution of arsenious oxide, or any material to be tested for arsenic, are added to the flask, arsine is formed, which is decomposed in the hot tube, a brown or black mirror being deposited beyond the heated portion. After a sufficient time, the whole of the arsenic is expelled from the solution as arsine, and by comparing the mirror with standard tubes prepared with known amounts of arsenious oxide (0·001–0·01 mgm.) a quantitative estimation may be made.

If the tube is not heated, but the gas kindled at the jet, the flame, which is tinged green, deposits black spots of arsenic on the outer surface of a glazed porcelain dish filled with water. These are produced by decomposition by the heat of the flame: $2AsH_3 = 2As + 3H_2$; they dissolve readily in a solution of sodium hypochlorite or bleaching powder (forming arsenates, *e.g.*, Na_3AsO_4), but are insoluble in tartaric acid. If a spot is moistened with yellow ammonium sulphide, and this evaporated by gentle heating, a *bright yellow* spot of arsenic trisulphide, As_2S_3, is left (*cf.* antimony hydride, p. 938).

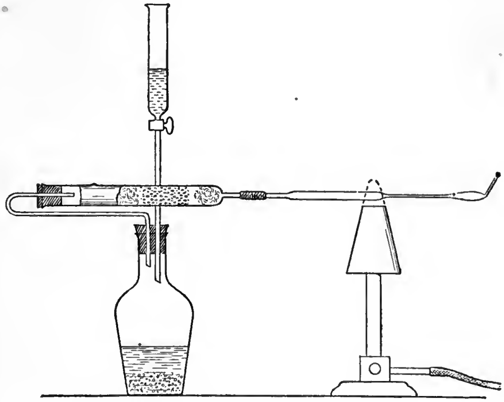


FIG. 325.—Marsh-Berzelius Test for Arsenic.

If arseniuretted hydrogen is passed into dilute silver nitrate solution, a black precipitate of metallic silver is formed, and the filtrate contains arsenious acid (*cf.* antimony, p. 939):

$$2AsH_3 + 12AgNO_3 + 6H_2O = 2H_3AsO_3 + 12HNO_3 + 12Ag.$$

If the solution of silver nitrate is more concentrated, no precipitate is formed, but a yellow solution of a double compound of **silver arsenide** and nitrate is obtained:

$$AsH_3 + 6AgNO_3 = Ag_3As{\cdot}3AgNO_3 + 3HNO_3.$$

On dilution with water, a black precipitate of metallic silver is deposited:

$$Ag_3As{\cdot}3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3AsO_3.$$

If the gas is passed into mercuric chloride solution, a yellow coloration is produced, due to the formation of $AsH(HgCl)_2$; on further treatment, this gives brown $As(HgCl)_3$, and finally black As_2Hg_3. This is the basis of the **Gutzeit test.**

The liquid is added to zinc and dilute sulphuric acid in a test-tube. A roll of lead acetate paper is placed in the tube to absorb H_2S, and a piece of filter-paper, soaked in mercuric chloride solution and dried, is stretched over the open mouth of the tube by a rubber band. The yellow stain is compared with standard stains produced with known amounts of arsenic. The test is very sensitive.

An ill-defined brown **solid hydride** is said to be formed by the action of water on sodium arsenide, by the action of the silent discharge on arsine, or by the electrolysis of dilute sulphuric acid with a cathode of arsenic. At 200° it is converted into grey arsenic. It has been given the formulæ As_4H_2, AsH_2, and $(AsH)_x$, but may be impure yellow arsenic. No definite hydride corresponding with N_2H_4 or P_2H_4 is known, but the organic compound **cacodyl,** $As_2(CH_3)_4$, is of this type.

Halogen compounds of arsenic.—The stable halogen compounds of arsenic, including the fluoride, are of the type AsR_3 (*cf.* phosphorus).

Arsenic trifluoride, AsF_3, a colourless fuming liquid, b.-pt. 60·4°, m.-pt. −8·5°, sp. gr. 2·66, is prepared by heating a mixture of arsenious oxide, powdered fluorspar, and concentrated sulphuric acid in a lead retort: $As_2O_3 + 6HF = 2AsF_3 + 3H_2O$. The water produced in the reaction is retained by the sulphuric acid, otherwise hydrolysis of the fluoride would occur: $2AsF_3 + 3H_2O \rightleftharpoons As_2O_3 + 6HF$. **Arsenic pentafluoride,** AsF_5, is obtained as a colourless gas, b.-pt. − 53°, m.-pt. − 80°, by distilling a mixture of the trifluoride, antimony pentafluoride, and bromine at a temperature not exceeding 55°, and collecting in a receiver cooled in liquid air: $AsF_3 + 2SbF_5 + Br_2 = AsF_5 + 2SbBrF_4$. The double salts K_2AsF_7,H_2O and $KAsOF_4,H_2O$ are formed as crystalline solids when potassium arsenate, K_3AsO_4, is dissolved in hydrofluoric acid.

Arsenic trichloride, $AsCl_3$, discovered by Glauber (1648), is the most important halogen compound of arsenic. It is formed when arsenic burns in chlorine gas—a reaction which occurs spontaneously even if the materials are very carefully dried—but is usually prepared by distilling a mixture of white arsenic, common salt, and concentrated sulphuric acid in a retort, and condensing the vapour in a cooled receiver: $As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$. The water is removed by the excess of sulphuric acid, otherwise hydrolysis would occur. The distillate is freed from excess of chlorine by distillation over powdered arsenic.

Arsenic trichloride is a colourless, oily liquid, b.-pt. 130°, m.-pt. − 18°, sp. gr. 2·2, which fumes in moist air, and is rapidly hydrolysed by water: the first product is a crystalline **hydroxychloride,** but with excess of water, arsenious acid (or its anhydride, As_4O_6) is formed:

$$(1)\ AsCl_3 + 2H_2O = 2HCl + AsCl(OH)_2;$$
$$(2)\ AsCl(OH)_2 + H_2O = As(OH)_3 + HCl.$$

The hydrolysis is reversible to a slight extent, showing that arsenic is approaching a metal in its properties (p. 450); if arsenious oxide is dissolved in hydrochloric acid and the liquid boiled, arsenious chloride distils over with the steam: $As_4O_6 + 12HCl \rightleftarrows 4AsCl_3 + 6H_2O$.

Arsenic oxychloride, $AsOCl$, is formed as a colourless fuming liquid by adding arsenic trioxide to the boiling trichloride. When heated, it gives $AsCl_3$ and a compound As_3O_4Cl. With water, it forms $AsCl(OH)_2$.

Arsenic pentachloride, $AsCl_5$, is said to be formed from the trichloride and chlorine at − 40°, but decomposes into its constituents above − 25°, and may be simply a solution of chlorine in the trichloride.

Arsenic tribromide, $AsBr_3$, is a colourless crystalline solid, m.-pt. 31°, b.-pt. 221°, less easily hydrolysed than $AsCl_3$, and **arsenic tri-iodide** forms red hexagonal crystals; both compounds are formed by heating arsenic with a solution of the halogen in carbon disulphide. The tri-iodide is only slightly hydrolysed by water, and is formed on adding a solution of arsenious oxide in hot hydrochloric acid to a solution of potassium iodide. A **di-iodide,** AsI_2, is obtained as a dark red mass by heating iodine with arsenic in a closed tube to 260°; it is soluble in carbon disulphide, but is decomposed by water into AsI_3 and arsenic. By heating AsI_3 with iodine to 150° a brown **pentaiodide,** AsI_5, is said to be formed. A brown **mono-iodide,** AsI, is produced as a brown powder when an alcoholic solution of iodine is saturated with arsenic.

Arsenious oxide. — **Arsenious oxide,** or **arsenic trioxide,** As_4O_6 (usually written As_2O_3), is the most important compound of arsenic; it is known in commerce as "white arsenic," or simply as "arsenic." It was known to the ancients, and used as a caustic. The intensely poisonous properties of the substance were first recognised by Paracelsus, doubtless from the results of his reckless use of arsenic as a medicine, and it was a favourite poison during the Middle Ages—the *aqua tofani*. It exists in three varieties:—(1) the **amorphous,** sp. gr. 3·738, m.-pt. 200°; (2) the **octahedral,** sp. gr. 3·689, sublimes without fusion; (3) the **rhombic,** sp. gr. 3·85, occurring as the mineral *claudetite.*

The vapour density of arsenious oxide between 570° and 1560° corresponds with the formula As_4O_6; at 1770° it is As_2O_3. In solution in nitrobenzene, the formula is also As_4O_6.

The **amorphous** variety is formed as a colourless transparent glass, first described by Roger Bacon, when the vapour is slowly condensed at a temperature slightly below its point of vaporisation, 218°. It may be preserved in sealed tubes, but at 100°, or in presence of moisture, it becomes opaque, and passes into the octahedral form. If the glass is dissolved in concentrated hydrochloric acid and the solution allowed to cool, crystals are deposited, each accompanied by a flash of light. The octahedral form is said not to exhibit this property (H. Rose). The vitreous form dissolves in about 25 parts of water at 10°, or in 12 at 100°, but the solubility diminishes on standing, owing to conversion into the octahedral form. The latter dissolves in about 70 parts of water at the ordinary temperature, but exceedingly slowly.

The **octahedral** is the stable form under ordinary conditions; it is produced when the vapour is *rapidly* condensed, when the trioxide is crystallised from water or hydrochloric acid, or spontaneously, with evolution of heat, from the vitreous form. It sublimes at 125–150°, but can be fused under increased pressure.

The **rhombic** variety is formed by crystallisation from a boiling saturated solution of the amorphous substance in caustic potash, or when the other varieties are heated for some time at 200°.

If arsenious oxide is heated in a sealed tube to 400°, the vitreous form remains at the bottom of the tube, the rhombic form sublimes to the intermediate part, and the octahedral form sublimes to the top of the tube. The different crystalline forms may be recognised under the microscope.

Arsenious oxide is easily **oxidised** to arsenic oxide, or arsenic pentoxide, As_2O_5, by ozone, hydrogen peroxide, chlorine, *aqua regia*, bromine, iodine, nitric acid, and hypochlorites (especially in alkaline solution); when arsenic acid or an arsenate is formed: $As_2O_3 + 2Cl_2 + 2H_2O = As_2O_5 + 4HCl$. It precipitates red cuprous oxide from Fehling's solution (p. 815).

Arsenious oxide is also easily **reduced** to arsenic by heating in a tube with charcoal, when a mirror of arsenic sublimes, or by a solution of stannous chloride, which gives a brown precipitate: $As_2O_3 + 3SnCl_2 + 6HCl = 3SnCl_4 + 2As + 3H_2O$. If arsenious oxide is boiled with hydrochloric acid and copper foil, the latter becomes grey, owing to deposition of arsenic:

$$As_2O_3 + 6HCl + 6Cu = As + 6CuCl + 3H_2O.$$

If the copper foil is now washed, dried, and heated in a tube, a crystalline sublimate of arsenious oxide is formed **(Reinsch's test)**.

By the action of fuming sulphuric acid on the trioxide, unstable sulphates, composed of As_2O_3 with 1, 2, 3, 4, 6, and 8 SO_3, are formed: As_2O_3 then acts as a feebly basic oxide. These are decomposed by water.

Small quantities of arsenious acid occur in some mineral waters, which are used as nerve tonics, and in improving the blood. Arsenious oxide is a violent poison: 0·06 gm. is a dangerous dose, and 0·125–0·25 gm. is fatal. Habitual use of small quantities renders the system immune to much larger doses, and the peasants of Styria are able to consume arsenious oxide in amounts (0·3 gm.) which would be fatal to those unaccustomed to its use. It is said by them to act as a cosmetic, to improve the breathing in mountain climbing, and to give plumpness to the figure. Freshly precipitated ferric hydroxide, obtained by adding magnesia to a solution of ferrous sulphate, absorbs arsenious oxide, and is the best antidote in cases of poisoning

Arsenious acid.—A solution of arsenious oxide in water has a feebly acid reaction; it probably contains **arsenious acid,** H_3AsO_3, or $HAsO_2$, although only the trioxide crystallises on cooling or concentration: $As_2O_3 + 3H_2O \rightleftharpoons 2As(OH)_3$. The acid is even weaker than sulphuretted hydrogen.

The finely-powdered oxide is not easily wetted by water, but a solution can be prepared by boiling. It also dissolves in warm sodium bicarbonate solution, with evolution of carbon dioxide, and formation of **sodium arsenite,** Na_3AsO_3, or $NaAsO_2$. This solution is often used for the standardisation of iodine solution. The latter oxidises the arsenite to arsenate: $As_2O_3 + 2I_2 + 2H_2O = As_2O_5 + 4HI$. The excess of bicarbonate has no action on the iodine, whilst if the arsenious oxide were dissolved in caustic alkali, the latter would react with iodine.

Three series of **arsenites** appear to exist, derived from the hypothetical acids:

*Ortho*arsenious acid, H_3AsO_3; *e.g.*,
K_3AsO_3, Ag_3AsO_3; $HCuAsO_3$, $Pb_3(AsO_3)_2$.
*Pyro*arsenious acid, $H_4As_2O_5$; *e.g.*, $Ca_2As_2O_5$; $(NH_4)_4As_2O_5$.
Meta-arsenious acid, $HAsO_2$; *e.g.*, $KAsO_2$, $Ba(AsO_2)_2$, $KH(AsO_2)_2$.

If arsenic trioxide is boiled with caustic alkali, carbonate or bicarbonate, alkali meta-arsenites, *e.g.*, $NaAsO_2$, are formed. Arsenic trioxide solution, neutralised with ammonia, gives with silver nitrate a yellow precipitate of **silver arsenite,** Ag_3AsO_3, soluble in acetic acid (the yellow silver phosphate, Ag_3PO_4, is insoluble). Copper sulphate added to the ammonium arsenite solution gives a bright green precipitate of **cupric hydrogen arsenite,** $CuHAsO_3$, known as **Scheele's green,** and formerly used for colouring wallpaper. When dissolved in ammonia, this salt is converted into cupr*ous* arsen*ate*. The brilliant pigment **Schweinfürter green,** which has the composition $Cu_3(AsO_2)_2,Cu(C_2H_3O_2)_2$, *i.e.*, a compound of cupric arsenite and cupric acetate, is obtained by boiling verdigris (a basic acetate of copper) with arsenious oxide and acetic acid.

Arsenic dioxide, AsO_2 (or As_2O_4), is said to be formed as a glass by heating equimolecular amounts of trioxide and pentoxide to 350°.

Arsenic pentoxide and arsenic acids.—Unlike phosphorus, arsenic on combustion in oxygen yields, not the pentoxide, but the trioxide. The latter may, however, be converted into **arsenic pentoxide,** As_2O_5, by oxidising agents (p. 379). It was prepared by Scheele (1775), by boiling white arsenic with concentrated nitric acid or *aqua regia* : it is formed on heating the residue from the preparation of nitrous anhydride (p. 587) :

$$As_2O_3 + 2HNO_3 = As_2O_5 + H_2O + N_2O_3.$$

The solution on cooling deposits rhombic crystals of **arsenic acid,** $2H_3AsO_4,H_2O$. At 100° these melt, lose water of crystallisation, and leave a crystalline powder of the composition $H_5As_3O_{10}$, or $3As_2O_5,5H_2O$. At 160° the acid slowly loses all the contained water and forms **arsenic pentoxide,** As_2O_5, as a deliquescent, white, crystalline solid. At 200° the water is eliminated in a much shorter time. The pyro- and meta-acids do not appear to exist, even in solution, but their salts are known.

Arsenic pentoxide melts at a red heat, and gives off oxygen : $2As_2O_5 = 2As_2O_3 + 2O_2$ (*cf.* P_2O_5,N_2O_5).

The **arsenates** are isomorphous with the phosphates, and probably have similar constitutional formulæ. The normal orthoarsenates exist in solution, as well as in the solid state, but the pyro- and meta-arsenates exist only in the solid condition, and are prepared by heating the acid and di-acid ortho-salts, as in the case of phosphates : $2Na_2HAsO_4 = H_2O + Na_4As_2O_7$; $NaH_2AsO_4 = NaAsO_3 + H_2O$. The salt $Na_2HAsO_4,12H_2O$ is largely used in calico-printing. Arsenic acid is an **oxidising agent ;** *e.g.*, it liberates iodine from potassium iodide and hydrochloric acid. It was formerly used in making aniline dyes.

Ammonium molybdate and concentrated nitric acid give with arsenates a yellow precipitate similar to that obtained with phosphates, but only on heating. Magnesia mixture (68 gm. of $MgCl_2,6H_2O$ and 165 gm. of NH_4Cl dissolved in 300 c.c. of water, 75 c.c. of ammonia, sp. gr. 0·88, added, and the whole made up to 1 litre) gives a white crystalline precipitate of **magnesium ammonium arsenate,** $MgNH_4AsO_4,6H_2O$, similar to $MgNH_4PO_4,6H_2O$. On heating, this leaves a residue of **magnesium pyroarsenate,** $Mg_2As_2O_7$.

The precipitate of magnesium ammonium arsenate is distinguished from the phosphate as follows. It is dissolved in dilute hydrochloric acid, and the hot solution treated with sulphur dioxide. Under these conditions all arsenates are reduced to arsenites, whilst phosphates are, of course, unacted upon : $As_2O_5 + 2SO_2 = As_2O_3 + 2SO_3$. The excess of sulphur dioxide is removed from the solution by boiling, and a current of sulphuretted hydrogen passed through the liquid. Yellow arsenious sulphide is precipitated. The filtrate is boiled to remove H_2S, and gives a precipitate of $MgNH_4PO_4,6H_2O$ when made alkaline with ammonia, if a phosphate is also present. Arsenates are also distinguished from phosphates by giving with silver nitrate in neutral solution a *chocolate-brown* precipitate of **silver arsenate,** Ag_3AsO_4, soluble in dilute nitric acid and in ammonia. Phosphates give a *yellow* precipitate of Ag_3PO_4. If an arsenite is present, it may be detected by dissolving the precipitate in dilute nitric acid, avoiding excess, and adding ammonia drop by drop. Brown silver arsenate is first precipitated, then yellow silver arsenite.

Sulphides and thioacids of arsenic.—The **trisulphide,** As_2S_3, and **disulphide,** As_2S_2, of arsenic occur native as the yellow and red minerals *orpiment* and *realgar*, respectively. They are prepared by heating arsenic or arsenic trioxide with sulphur in proper proportions, *e.g.*, $2As_2O_3 + 7S = 2As_2S_2 + 3SO_2$. The **disulphide** is also made at Freiburg by distilling iron pyrites with arsenical pyrites: $2FeS_2 + 2FeAsS = As_2S_2 + 4FeS$. The **trisulphide** is easily prepared by passing sulphuretted hydrogen through a solution of arsenic trioxide in dilute hydrochloric acid:

$$2AsCl_3 + 3H_2S = As_2S_3 + 6HCl.$$

If sulphuretted hydrogen is passed into a solution of arsenious oxide in boiling distilled water, no precipitate is formed, but a yellow **colloidal solution** of arsenic trisulphide is produced (p. 12). Addition of dilute hydrochloric acid, or salts, to this at once brings about coagulation, and yellow flocks of As_2S_3 separate. If these are at once filtered off and washed, they again pass into colloidal solution when the acid or salt has been washed out, but if they are allowed to stand for some time in the solution in which they have been precipitated, they become quite insoluble.

Realgar is used in pyrotechny. *Bengal fire* is a mixture of 27 parts of nitre, 7 parts of sulphur, and 2 parts of realgar. Mixed with slaked lime, it is used as a depilatory in tanning to remove hair from hides; a mixture of orpiment and slaked lime is also used for removing superfluous hair under the name of "Rusma." In both cases the active agent is probably calcium hydrosulphide, $Ca(SH)_2$, which dissolves hair. A mixture of orpiment (the *auri pigmentum* of the Romans) with the trioxide, obtained by subliming the latter with sulphur, is used as a pigment under the name of *King's yellow.*

Both sulphides of arsenic burn when heated in air, forming sulphur dioxide and arsenic trioxide. They are oxidised by nitric acid, but are insoluble in concentrated hydrochloric acid. (Sb_2S_3 is soluble.) Since they are not dissolved by the dilute hydrochloric acid of gastric juice, the sulphides of arsenic are not poisonous.

Arsenic pentasulphide, As_2S_5, is said to be formed when sulphuretted hydrogen is passed rapidly into a warm solution of arsenic acid containing 10–12 per cent. of free hydrochloric acid;

if the reaction takes place slowly a mixture of trisulphide and sulphur is deposited: $As_2O_5 + 5H_2S = As_2S_3 + 2S + 5H_2O$. The first product is the unstable thioarsenic acid, H_3AsO_3S. In qualitative analysis, solutions of arsenates are reduced with sulphurous acid before treating with sulphuretted hydrogen, as the reduction with the latter is a very slow process.

Arsenic trisulphide dissolves readily in caustic potash, soda, or ammonia, and even in a warm solution of ammonium carbonate (antimony trisulphide is insoluble in the latter). The product is a mixture of an arsenite and a **thioarsenite**:

$$As_2S_3 + 4KOH = K_2HAsO_3 + K_2HAsS_3 + H_2O.$$

If an acid is added, the whole of the arsenic is precipitated as sulphide:

$$K_2HAsO_3 + K_2HAsS_3 + 4HCl = 4KCl + 3H_2O + As_2S_3.$$

If arsenic trisulphide is dissolved in an alkali-sulphide, a thioarsenite alone is formed:

$$K_2S + As_2S_3 = 2KAsS_2; \quad \text{or} \quad 3K_2S + As_2S_3 = 2K_3AsS_3.$$

The compounds $(NH_4)_3AsS_3$ and $Ca_3(AsS_3)_2$ form colourless crystals: K_3AsS_3 and Na_3AsS_3 are amorphous white powders. Thioarsenites are derived from hypothetical thioarsenious acids: H_3AsS_3 (*ortho*); $H_4As_2S_5$ (*pyro*); $HAsS_2$ (*meta*). Berzelius, who first prepared the salts, recognised that, in them, sulphur takes the place of oxygen as the "acidifying principle."

If arsenious sulphide is dissolved in an alkali polysulphide, *e.g.*, yellow ammonium sulphide, $(NH_4)_2S_2$, or if a thioarsenite is digested with sulphur, a yellow solution of a **thioarsenate** is obtained: $K_3\overset{\text{III}}{As}S_3 + S = K_3\overset{\text{V}}{As}S_4$. On acidifying the solution, a yellow precipitate is thrown down, which has been variously described as the pentasulphide and as a mixture of the trisulphide and sulphur. Arsenic trisulphide and sulphur, when digested with caustic potash, form salts containing both oxygen and sulphur; *e.g.*, $Na_3AsOS_3,12H_2O$; K_3AsOS_3; $Na_2HAsOS_3,8H_2O$; $Na_3AsO_2S_2,11H_2O$. These are all colourless, and are decomposed by acids into arsenic acid and free sulphur, or arsenic trisulphide.

The thioarsenates are soluble, and crystalline; *e.g.*, $Na_3AsS_4,8H_2O$; $(NH_4)_3AsS_4$. By the action of sodium sulphide solution on arsenious oxide in the proportions $2Na_2S : As_2O_3$, a thioarsenate and elementary arsenic are produced.

EXERCISES ON CHAPTER XXXII

1. What are the chief sources of white arsenic? How may this be converted into: (*a*) arsine, (*b*) arsenic trichloride, (*c*) arsenic acid, (*d*) arsenic trisulphide?

2. By what reactions is arsenic hydride formed? How is its formation used as a test for arsenic? What other tests for arsenic are applied?

3. How are arsenites and arsenates prepared? Compare the properties of arsenious and arsenic acids with the corresponding acids of nitrogen and phosphorus. How is arsenic acid distinguished from phosphoric acid in analysis?

4. Give examples of oxidising and reducing reactions of arsenious oxide. What happens if sulphuretted hydrogen is passed through an aqueous solution of this substance?

5. In what forms does arsenious oxide exist? What happens when it is (*a*) heated with charcoal, (*b*) treated in solution with sodium amalgam, (*c*) treated with bromine water?

6. What reactions take place when arsenic trisulphide is (*a*) boiled with caustic soda, (*b*) digested with yellow ammonium sulphide? If the products are acidified, what substances are formed? Give equations.

7. What is the action of water on (*a*) arsenic trichloride, (*b*) phosphorus pentabromide, (*c*) arsenic pentoxide?

8. One hundred c.c. of a gas are collected over mercury in a tube closed above by a plaster of Paris plug. On standing, diffusion occurs, and when the mercury level again becomes constant it is found to correspond with 164 c.c. What is the molecular weight of the gas? One hundred c.c. of the gas on heating with sodium gave 150 c.c. of hydrogen. What is the gas?

CHAPTER XXXIII

CARBON AND THE HYDROCARBONS

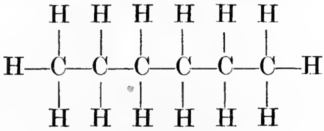
Carbon and its compounds.—The element **carbon** is found in Nature in a diversity of forms, both in the free state and in combination. Elementary carbon occurs in the crystalline forms of **diamond,** and **graphite** (also called *plumbago,* and *black-lead*); and amorphous as **anthracite coal.** Free carbon also occurs in meteorites, and the spectroscope shows its presence in the cooler stars. In the form of **cyanogen,** C_2N_2, carbon occurs in the sun, and **hydrocarbons,** or compounds of carbon and hydrogen, are constituents of some stars (p. 32). Mixtures of these hydrocarbons compose mineral oil, or *petroleum,* which issues from the earth in enormous quantites in Baku (Russia), and Pennsylvania (America). Other oil-fields are Galicia, Mexico, Burma, Ontario, and Mesopotamia. *Coal* contains complex hydrocarbons, but oxygen and nitrogen are also present. **Carbon dioxide,** CO_2, occurs uncombined, *e.g.,* in the atmosphere, and as **carbonates,** especially **calcium carbonate,** $CaCO_3$ (*chalk, limestone,* and *marble*), as **magnesium carbonate,** $MgCO_3$ (*magnesite*), or a compound of the two, $CaCO_3,MgCO_3$, known as *dolomite,* of which whole mountain-chains are constituted.

The bodies of plants and animals contain compounds of carbon with hydrogen and oxygen, and sometimes nitrogen, sulphur, and phosphorus. These so-called **organic compounds** comprise:

(1) **Carbohydrates** such as **starch,** $C_6H_{10}O_5$; various **sugars,** such as glucose, or **grape-sugar,** $C_6H_{12}O_6$, and saccharose, or **cane-sugar,** $C_{12}H_{22}O_{11}$; and **cellulose,** $C_6H_{10}O_5$, or woody-fibre, all occurring in plants; (2) **proteins,** such as albumin, gelatin, and a number of very complicated compounds occurring both in plants and animals, which contain nitrogen, and usually sulphur and phosphorus, in addition to carbon, hydrogen, and oxygen. The great number of these carbon compounds, many of which have been prepared by **synthesis** from the elements, makes it necessary to consider them in a special branch of the science known as **organic chemistry.**

The fact that carbon forms such a large number of compounds is due to the facility with which its atoms, unlike those of other elements, combine to form **chains,** which may have branches **(aliphatic,** or **fatty, compounds)**; or **rings (cyclic,** or **aromatic, compounds).** Examples of such compounds are :

Hexane :
b.-pt. 69°.



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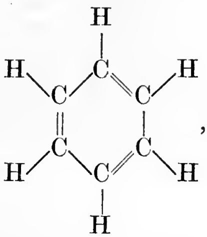
, contained in petrol (*aliphatic*).

Benzene :
b.-pt. 80·4°.



, contained in coal tar (*cyclic*).

By means of the *X*-ray method (p. 1018), the diameter of the benzene ring has been estimated at $12{\cdot}4 \times 10^{-8}$ cm.; its thickness at $1{\cdot}19 \times 10^{-8}$ cm.

Allotropic forms of carbon.—Carbon is one of the most striking examples of **allotropy.** The majority of organic compounds, when heated without access of air, blacken, or char, evolve steam and various volatile organic compounds, and usually inflammable gases (*e.g.*, methane, CH_4), leaving finally a black residue of **charcoal,** which, if a compound free from mineral matter and containing only carbon, hydrogen, and oxygen (*e.g.*, sugar, or cellulose) is used, consists almost solely of carbon. The smoke produced on burning oils with an insufficient supply of air also consists mainly of particles of carbon. That charcoal should be, chemically, the same substance as the **diamond** would appear highly improbable to one unacquainted with the fact; its analogy with graphite, or black-lead, would seem clearer, by reason of the colour, yet it is curious that the composition of the diamond was elucidated (1775) before that of graphite (1800). The identity of the three forms of carbon was established by showing that equal weights of the pure substances, when burnt in oxygen, yield identical weights of carbon dioxide, no other substance being produced. The amounts of heat liberated in the three cases, however, are different: for 12 gm. of carbon they are :

graphite :	94·26 kgm. cal.
diamond :	94·43 kgm. cal.
charcoal :	97·65 kgm. cal.

These differences are supposed to be due to different modes of linkage of the carbon atoms in the molecules of the substances. It is further assumed, on account of the extremely high temperature at which carbon volatilises (the boiling point has been given as 3600°), and from other considerations, that the molecules are highly polymerised, $(C)_n$. Recent experiments, however (p. 1019), indicate that the diamond consists of an assemblage of single atoms of carbon, united one to the other by four valencies in space.

The diamond.—This mineral, which in its transparent varieties forms the most beautiful and costly gem, has been known from very early times. It is found, as yellow rounded "pebbles," in India, Brazil, New South Wales, Arkansas, and particularly at Kimberley, in British South Africa. Most diamonds are small, but the Cullinan diamond, discovered at Kimberley in 1905, weighed about $1\frac{1}{3}$ lb., viz., $3025\frac{3}{4}$ carats (1 *carat* = 0·2054 gm.); this is the largest yet discovered, and was cut into two brilliants of 516 and 309 carats.

Large colourless diamonds are the Pitt diamond (136·25 carats), and the Koh-i-noor, originally 186 carats, but reduced to 106 by re-cutting. The Hope diamond, 44·5 carats, is a fine blue stone, valued at £25,000. The cause of the colour of diamonds is not clear: exposure to cathode rays deepens the colour, which is lost on heating to 300–400°.

Black diamonds, known as *carbonado*, and *bort*, are of no value as gems, but are very hard, and are used for rock-drills, and, when crushed, for cutting and polishing clear diamonds. The latter are pressed against a revolving metal disc, covered with diamond powder and oil.

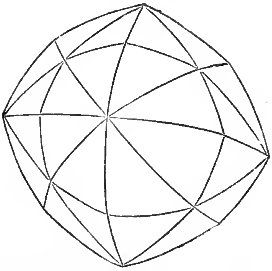


FIG. 326.—Diamond Crystal.

The diamond crystallises in the regular (or cubic) system; forms related to the cube or the octahedron, sometimes with curved faces, predominate (Fig. 326). The curved faces appear to have been formed by the action of a solvent. By cutting, however, the natural crystalline form is obliterated, and an artificial shape, which gives rise to a large amount of internal reflexion, producing the "fire" of the stone, is impressed upon it. The "brilliant," for example, consists of one larger flat face, forming the base of a many-sided pyramid (Fig. 327).

Indian diamonds occur in river gravels and alluvial deposits, and are separated by washing. They appear to have been transported by water. At Kimberley the diamonds occur *in situ* in the original rock ("blue-ground "), which is a weathered form of olivine, and runs in large "pipes" downwards through the earth, cutting through strata of sand, rock, and quartz. Masses of this earth are blasted out and allowed to weather, when they crumble to light earth and a small quantity of heavier mineral, consisting of pyrites, calcite, tourmaline, garnets, ekladite, and, possibly, diamonds. The light material is washed off, and the heavier residue carried by water over a bed of grease: to this the diamonds adhere. The yield is variable; in the richest mines it is about 0·1 gm. per ton of earth.

The diamond is extremely hard, although fairly brittle: it is scratched by no other substance (except possibly boron carbide, B_6C), and stands highest in **Moh's scale of hardness,** which comprises the following minerals :—

1. Talc.
2. Gypsum.
3. Calcite.
4. Fluorite.
5. Apatite.
6. Orthoclase.
7. Quartz.
8. Topaz.
9. Corundum.
10. Diamond.

Each mineral in the scale is scratched by all those below it. In reality, the diamond is about 140 times harder than corundum.

The diamond has a high refractive index (2·417 for the D-line), a density of 3·0–3·52, and a high dispersive power, exhibiting a play of colours in white light. It is transparent to *X*-rays, whilst all imitations are opaque. Diamonds are used for cutting glass; for this purpose a chisel-shaped crystal-edge is necessary, since a splinter merely scratches glass without cutting it.

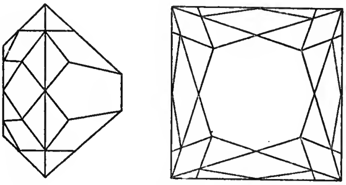


FIG. 327.—Diamond cut as "Brilliant."

The diamond resists the action of almost all chemical reagents; a mixture of potassium dichromate and sulphuric acid oxidises it slowly at 200° to carbon dioxide. When strongly heated in the arc, with exclusion of air, it is only superficially transformed into graphite, which is the stable form at high temperatures, and is produced from diamond and amorphous carbon alike. If heated to 700–900° in air or oxygen, the diamond burns, leaving only a trace of ash (0·02–0·05 per cent., chiefly silica and oxide of iron); bort may leave as much as 4 per cent. of ash. Diamonds are attacked by fused sodium carbonate.

The combustibility of the diamond was foreshadowed by Newton, who, arguing from the similarity of its refractive index to those of oil of turpentine, camphor, and amber, suggested that it might be "an unctuous [oily] substance coagulated." The Florentine Academicians in 1694 heated a diamond in the focus of a powerful burning-glass: it glowed like a red-hot coal and disappeared. D'Arcet (1766) found that, when a diamond was strongly heated in a *closed* crucible, it remained unchanged. Davy and Faraday in 1813, using the original Florentine lens, burnt a diamond in oxygen. It took fire, and continued to burn, even if removed from the focus, with a steady brilliant light. Nothing was produced but carbon dioxide, which rendered lime-water milky. Tennant (1797) was able to burn diamonds by strongly heating them with fused nitre in a gold tube: he found that as much carbon dioxide was formed as Lavoisier had obtained from an equal weight of charcoal.

Expt. 264.—The combustion of the diamond in oxygen may be exhibited by heating a splinter of *carbonado* to whiteness by an electric current in a spiral of fine platinum wire supported by copper leads inside a jar of oxygen (Fig. 328). A little lime-water is shaken up with the gas afterwards.

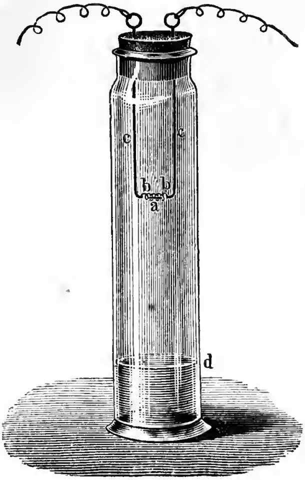


Fig. 328.—Combustion of the Diamond in Oxygen.

After many unsuccessful attempts to prepare diamonds artificially, the problem was to some extent solved by Moissan in 1893. He heated charcoal with iron in the electric furnace to a very high temperature. Fused iron dissolves carbon (p. 982); on cooling the iron slowly most of the carbon deposits in the form of scales of graphite, which are seen in a broken piece of grey cast-iron. When the iron is rapidly quenched, under ordinary conditions, the carbon remains in solid solution as the carbide, Fe_3C, and white cast-iron is produced. Moissan cooled the iron containing carbon suddenly from 3500° to 350° by plunging the crucible, taken from the electric furnace, into water or molten lead. The outer portion solidified at once, and the still liquid portion imprisoned within it solidified in due course. On dissolving away the iron with hydrochloric acid, a residue was left containing three varieties of carbon: (1) a small amount of graphite; (2) curious brown twisted threads, apparently formed under great pressure; and (3) a denser portion which contained microscopic diamonds, some black and some transparent. It was usually considered that the important condition in Moissan's experiment was the enormous pressure developed by the solidification of the molten cast-iron inside the rigid outer skin which was first formed, but Sir C. L. Parsons (1918) believes, from numerous experiments, that the function of this skin is to prevent the escape of occluded gases such as carbon monoxide, the presence of which is essential to the formation of diamonds.

The presence of oxide of iron in diamond-bearing earth suggests that a process similar to that used by Moissan may have been responsible for the origin of the natural diamonds. Small clear diamonds have been found in meteorites, and diamonds may be of celestial origin: the iron may, however, have come from the interior of the earth.

Graphite.—Prior to 1779, molybdenum sulphide (MoS_2) and graphite (C) were confused together under the name *molybdœna*, or *black-lead*, since both were soft black minerals with a metallic lustre, giving a streak on paper, similar to that produced by lead. Scheele, in that year, found that the former mineral gave a peculiar solid acid (molybdic acid, MoO_3) when roasted in the air, evolving sulphur dioxide; the name molybdena was reserved for this mineral, whilst the other was called **graphite** (Greek *grapho*—I write), **plumbago, or black-lead,** and considered to be a carbide of iron, since it usually left a residue of oxide of iron when burnt, carbon dioxide being formed. Scheele noticed that graphite deposits from molten iron in blast furnaces. This variety is called *kish*. In 1800, however, Mackenzie burnt graphite in oxygen and found that it yielded almost as much carbon dioxide as an equal weight of pure charcoal. The idea that it contained iron was not definitely given up until perfectly pure graphite was first prepared by Brodie in 1859, after which it was recognised as merely an allotropic form of carbon.

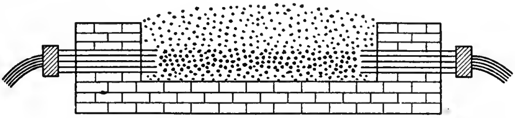


FIG. 329.—Manufacture of Graphite in the Electric Furnace.

Graphite is found in Borrowdale (Cumberland), Siberia, Ceylon, India, and Bohemia; enormous beds, 20–30 ft. thick, of nearly pure graphite are found in the Eureka Black Lead Mines, California. It is supposed to be of organic origin (see Coal). About 80,000 tons are mined annually. Ceylon and Siberia supply most of the European graphite.

Graphite is produced artificially on the large scale by the Acheson process at Niagara: 2,500 tons were made in 1915. A mixture of sand and powdered anthracite or coke (petroleum coke is best) is heated very strongly for twenty-four to thirty hours by an electric current. Carbon rods lead the current through the mass, which is supported in a brick furnace and covered with sand (Fig. 329).

Apparently silicon carbide (*carborundum*) is first formed, and then decomposed at the very high temperature, the silicon being volatilised : (1) $SiO_2 + 3C = SiC + 2CO$: (2) $SiC = Si + C$ (graphite).

The product is very pure and soft, and free from grit. If treated with water containing tannin, it forms a colloidal suspension, used as a lubricant under the name of *deflocculated graphite*, or " aquadag " : when kneaded with oil, the water is squeezed out and the suspension of graphite in oil is called " oildag " (" dag " = deflocculated Acheson graphite).

Graphite crystallises in grey, shining hexagonal plates, belonging to the monoclinic system, which when rubbed flake off in thin layers ; hence it has a greasy feel, makes a streak on paper, and acts as a lubricant. It is also used (as " black-lead ") in polishing iron work and granular gunpowder. An amorphous variety exists. Graphite has a specific gravity of 2·1–2·6, and is a good conductor of heat and electricity : on account of the latter property it is used in the cores of arc-carbons (p. 684), as anodes for electrolytic cells, and for covering plaster moulds on which copper is deposited by the electrotyping process (p. 809). Graphite burns only at a high temperature (about 690° in air), and, on account of its refractory character, is used for making plumbago crucibles : these consist of 75 parts of plastic clay, 25 parts of sand, and 100 parts of graphite, moulded and baked. A granular mixture of graphite, carborundum, and clay is used as a resistance in electric furnaces under the name of *kryptol.* Mixed with a little plastic clay, and squirted into threads, graphite is used in the manufacture of black-lead pencils.

Graphite is not attacked by dilute acids, or fused alkalies, or when heated in chlorine. A mixture of potassium dichromate and sulphuric acid slowly oxidises it to carbon dioxide. When moistened with concentrated nitric acid and then heated, some varieties of graphite (Borrowdale and Austrian) swell up : others (Ceylon and American) do not. This is known as **Luzi's test** (1891).

The action of concentrated nitric acid on graphite is peculiar ; whereas the diamond is not attacked by this reagent, and amorphous charcoal is oxidised to dark brown soluble substances containing **mellitic acid,** $C_6(CO_2H)_6$ (Hatchett, 1805), and ultimately to carbon dioxide, graphite is converted into a peculiar green or yellow, almost insoluble, acid substance, known as **graphitic acid** (Brodie, 1859). A mixture of nitric acid, potassium chlorate, and sulphuric acid is usually employed as an oxidising agent.

Graphitic acid is very sparingly soluble in pure water, and reddens moist litmus paper : it is microscopically crystalline or amorphous, and has the formula $C_{11}H_4O_5$. On heating it swells up and leaves a fine black powder of **pyrographitic oxide,** $C_{22}H_2O_4$. When treated with hydriodic acid, graphitic acid takes up hydrogen, forming

hydrographitic acid, which does not yield pyrographitic acid on heating.

A mixture of potassium chlorate and concentrated sulphuric acid converts graphite into a black substance containing hydrogen, oxygen, and sulphuric acid, called **graphon sulphate** by Brodie. On heating, this swells up, evolves gas, and then falls to a fine powder of **pure graphite** (sp. gr. 2·25). If this is thrown on water, the impurities sink, and the pure graphite remains floating on the surface.

Amorphous carbon.—The following varieties of **amorphous carbon** are usually described :

1. **Charcoal :** from wood, sugar, etc. 2. **Lampblack :** soot, acetylene black. 3. **Animal charcoal :** bone-charcoal, ivory black. 4. **Coke** (coal, anthracite, etc.). 5. **Gas carbon.** 6. **Electrode carbon :** arc carbons, etc. (artificial).

They are all black and opaque, the density and hardness depending largely on the temperature at which they were formed. The *X*-ray spectra show that they are all really microcrystalline, with the same arrangement of the atoms as in graphite.

Charcoal.—The black residue, rich in carbon, obtained by heating vegetable substances, such as wood or sugar, with exclusion of air, is known as **charcoal.** The purest variety is obtained by heating recrystallised cane-sugar in a large covered crucible until gases cease to be evolved; the resulting charcoal is heated to 1000° in a graphite tube in a current of chlorine to remove residual hydrogen as hydrogen chloride, after which it is washed and ignited in hydrogen to remove chlorine. Charcoal so prepared has a density of 1·8, and ignites in air at 450°. Pure amorphous carbon is also produced, mixed with magnesia, by burning magnesium in carbon dioxide : it is free from hydrogen.

The low ignition temperature of charcoal, as compared with the other forms of carbon, is seen from Moissan's results :

	Diamond.	Graphite.	Wood charcoal.
Evolution of carbon dioxide begins...	720°	570°	200°
,, ,, ,, abundant	790°	600°	—
Burns with flame	800–850°	690°	345°

Wood charcoal is largely used as fuel in countries where wood is abundant. It is prepared by the **destructive distillation of wood,** *i.e.*, the decomposition of the latter into volatile parts (gas, water, acetic acid, acetone, and tar), and non-volatile charcoal.

Dry wood on heating to 220° becomes brown, at 280° deep brown, at 310° brown and friable; above 350°, black charcoal is produced. The destructive distillation of wood, with production of tar, acid, and spirit, was examined by Glauber in the seventeenth century. The percentage of carbon in the charcoal never exceeds 78 when heated to redness under ordinary pressure. By heating above 1500°, the residual hydrogen falls to 0·62 per cent.

The manufacture of charcoal is carried out in : (*a*) pits or heaps (*meiler*), (*b*) closed ovens or retorts. The charring of wood in meiler, ordinary **charcoal burning,** is very old. A rough central chimney is built of turf, and billets of wood stacked round it in a conical pile, the whole being covered in with turf (Fig. 330). A lighted faggot is dropped down the chimney, to kindle the wood, which burns *slowly*, just sufficient air being admitted through holes at the bottom. A part of the wood burns, and the heat generated chars the rest. After some days the luminous flame from the chimney is replaced by a blue flame of carbon monoxide. All the air-holes are now stopped up, and the charcoal allowed to cool. About 24 per cent. of the weight of the wood is obtained as charcoal ; all the volatile products are lost.

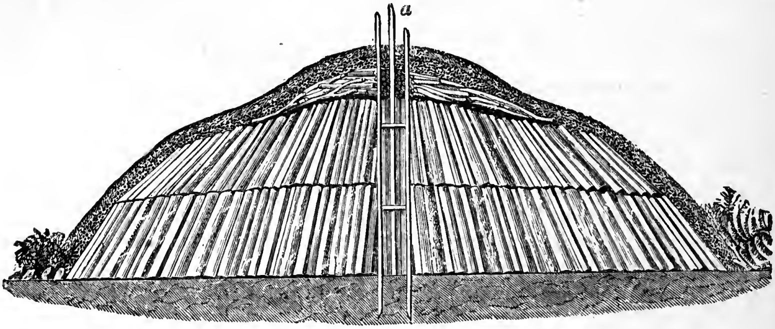


FIG. 330.—Charcoal " Meiler."

In the modern process, based on Glauber's work, the wood is heated in externally fired ovens, or iron retorts, from which air is excluded. The volatile liquid products are collected, and the inflammable gas is used for heating the retorts. The liquid distillate consists of (*a*) a watery portion, the **pyroligneous acid,** containing water, acetic acid, methyl alcohol, and acetone, which are extracted ; (*b*) tar, which is valuable (*e.g.*, Stockholm tar, from pinewood). The yields, from 100 parts of dry wood, are, by weight : charcoal 25, tar 10, pyroligneous acid 40, gas 25,

Properties of charcoal.—Wood charcoal is a black, amorphous, friable material, retaining more or less the original shape of the wood, but diminished in volume. Although the specific gravity of air-free charcoal is 1·4–1·9, the mass is very porous, and floats on water. If the air is removed by placing the charcoal in water in a bottle connected with an air-pump, the charcoal gives out bubbles and slowly sinks. Charcoal is very permanent on exposure to air and moisture; charred oak stakes, planted in the bed of the Thames by the Britons to resist the advance of Julius Cæsar, were found nearly two thousand years later, in the exact spot indicated by Tacitus, and still sound at heart.

In virtue of its great porosity, charcoal readily **absorbs** (or **adsorbs**) **gases** (Scheele, and Fontana, 1777).

EXPT. 265.—If a piece of recently ignited wood-charcoal is passed into a tube of ammonia gas standing over mercury (Fig. 331), the gas is rapidly absorbed; the charcoal takes up about 90 times its volume of ammonia gas.

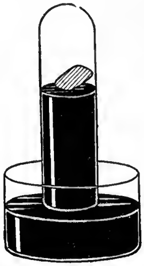


FIG. 331.—Absorption of Ammonia Gas by Charcoal.

A very active form of charcoal is prepared by heating the shell of the cocoanut; 1 volume of such charcoal, quenched under mercury, absorbs the following volumes of different gases (reduced to S.T.P.) at the ordinary temperature:

Ammonia	171·7	Hydrogen phosphide	69·1
Cyanogen	107·5	Carbon dioxide	67·7
Nitric oxide	86·3	Carbon monoxide	21·2
Ethylene	74·7	Oxygen	17·9
Nitrous oxide	70·5	Nitrogen	15

The preferential absorption of ethylene by charcoal is applied in its extraction from coal gas. Vapours of volatile liquids are absorbed even more readily than gases: the volumes of ammonia, carbon dioxide, steam, and alcohol vapour absorbed at 126·5° are 21·9, 16·6, 43·8, and 110·8, respectively. Generally speaking, the absorption increases the nearer the gas or vapour is to its point of liquefaction at the temperature of the experiment, and this supports Faraday's theory (p. 198), that the gas is held by the charcoal in a highly condensed, possibly liquid, layer upon its surface. McBain finds that the amount of gas taken up increases slowly with lapse of time, due to a slow penetration of the condensed layer into the interior (p. 197). At low temperatures the absorbed amount increases rapidly (Dewar, 1904):

Gas	H_2	N_2	O_2	A	He	
0°	4	15	18	12	2	volumes
−185°	35	155	230	175	15	,,

In this way high vacua (p. 193) may be produced, and gases separated from one another.

Expt. 266.—The condensed layer of gas held by the charcoal is very reactive (Stenhouse, 1855). Place a crucible containing powdered, recently ignited, charcoal in a jar of sulphuretted hydrogen. After it has become saturated with the gas, transfer it to a jar of oxygen. Ignition occurs.

Chlorine absorbed by charcoal unites with hydrogen passed over it in the dark; carbon monoxide and chlorine, or sulphur dioxide and chlorine, unite when passed over charcoal, which acts as a *catalyst,* to form carbonyl chloride, $COCl_2$, and sulphuryl chloride, SO_2Cl_2.

Charcoal also takes up many substances, *e.g.*, metallic salts, and organic substances such as alkaloids (*e.g.*, quinine), and colouring matters, from *solutions* (Lowitz, 1790). It removes fusel oil (amyl alcohol) from crude spirit.

Expt. 267.—Boil solutions of litmus and indigo with finely-powdered animal charcoal, and filter. The filtrates are colourless.

Animal charcoal.—This material, also known as *bone-black,* is prepared by the destructive distillation of bones in iron retorts. The volatile products are: (*a*) a watery liquid which, unlike that from wood, is alkaline, and contains ammonia and nitrogenous organic bases; (*b*) gases, and (*c*) *bone-oil* or *Dippel's oil* (containing pyridine, etc.). The residue in the retort is a black mass containing about 10 per cent. of amorphous carbon disseminated through a very porous substrate, consisting of 80 per cent. of calcium phosphate (p. 609), together with calcium carbonate, etc. If the phosphate and other salts are dissolved out by hydrochloric acid, the charcoal remains as **ivory black.**

Animal charcoal is largely used to decolorise sugar syrup, a process introduced by Derosnes in 1812. This is an adsorptive action, and is carried out by allowing the syrup to trickle through towers 25–30 ft. high filled with small pieces of bone-black. When the latter has become inactive, it is revived by reheating in retorts. Finally it is burnt, yielding *bone-ash* (p. 609). **Blood charcoal** is used for the same purpose.

Lampblack.—When carbonaceous fuels such as coal, wax, oil, and turpentine (but not charcoal) are burnt with a supply of air insufficient for complete combustion, part of the carbon separates in the form of particles, forming **smoke,** which settles out on solid surfaces as **soot.** A fine variety of soot, called **lampblack,** is prepared as a pigment by burning turpentine, tar, etc., in a limited supply of air, and collecting the soot by deposition on coarse blankets, or by electrostatic precipitation. In America, natural gas is burnt under a cooled, rotating metal disc, from which the lampblack is removed by scrapers.

A very fine variety of lampblack, for use as a pigment, is prepared by the spontaneous explosion of acetylene under 6 atm. pressure; pure hydrogen is produced at the same time: $C_2H_2 = 2C + H_2$.

Lampblack contains up to 20 per cent. of oily impurities, which may be removed by ignition in chlorine and hydrogen, as in the case of sugar charcoal (p. 665); it is then a very pure form of carbon. The density of lampblack is 1·78.

Coal.—The two varieties of amorphous carbon, **coke** and **gas carbon,** are derived from **coal,** and since some varieties of coal **(anthracite)** contain more than 90 per cent. of carbon, they will be considered here.

Coal is a carbonaceous mineral, which is the final result of a series of decompositions (which have occurred in the presence of a limited supply of air) undergone by vegetable matter of the remote past. High pressure, due to the weight of superimposed strata, was probably also necessary in these changes. A portion of the carbon, hydrogen, and oxygen was eliminated as carbon dioxide, water, and methane (CH_4), and the residue became increasingly rich in carbon. The early stages of the decomposition of the vegetable matter were probably caused by bacteria, and heating under pressure may have played a part in the later stages. Distinct evidence of vegetable remains in coal is disclosed by microscopic examination, and fossil trees and plants are often found in the seams. The character of the vegetable matter, and the manner in which it was covered by earthy deposits, probably varied from case to case. Two theories have been advanced to explain the origin of coal. Large beds of coal are supposed to have been deposited *in situ* from vegetable remains; impure current-bedded local coal, such as cannel, is regarded as derived from the burying of water-borne vegetable matter in a delta.

Stopes, from microscopic investigations, has recognised four constituents in banded coal, viz., *durain, fusain, vitrain,* and *clarain.* Although chemical methods have not given much useful information as to these constituents of coal, their behaviour on coking, *i.e.*, on heating out of contact with air, has been shown by Lessing to be different. Fusain yields a powdery coke; in the case of durain the coke is also very friable, whilst with clarain fusion and swelling occur, with formation of a brown coherent coke. Vitrain also undergoes fusion, yielding a silver-white coke, which exhibits excrescences.

Since the separation of the constituents of banded coal is a matter of great difficulty, users of that fuel are more interested in the various types of coal as they come from the mine; although these may be very heterogeneous, it is possible to give a broad general classification of coals, based on their behaviour during combustion or gasification.

The first stage in the conversion of vegetable matter into coal is represented by **peat,** which consists of accumulations of vegetable matter, chiefly mosses and bog-plants, which have undergone partial change, and still preserve evidences of organic structure, although the deeper layers may be more compact and homogeneous. The next stage is represented by **lignite,** or **brown coal,** which is more compact than peat, and is lustrous, although impressions and remains of vegetable fragments, leaves, etc., are still distinct and numerous. Large beds of lignite occur, near the surface, in many parts of Germany, Hungary, and the Mississippi Valley, and are utilised as a cheap steam-raising fuel. **Jet** is a hard variety of lignite, used for ornaments.

The next stage of the process leads to the very important types of **bituminous coal,** *i.e.*, common coal. These, as mentioned above, are complex : distinct evidences of vegetable origin are still present, and the original plants are sometimes found fossilised. Bituminous coals burn with a bright smoky flame, and are further divided into **caking** and **non-caking** coals, according as they do or do not soften and fuse together on burning or coking. **Cannel coal** is a compact, non-lustrous, variety, dull grey or black in colour, breaking with a conchoidal fracture, and yielding a large amount of gas and little coke. Splinters of cannel coal burn like candles when ignited, hence the name.

The latest stages in coal-formation consist chiefly of carbon, and are known as **anthracite.** Anthracite has a high ignition point, usually a brilliant lustre, and a conchoidal fracture, and does not burn with a flame. It is used in firing ships' boilers, since it gives an intense heat on combustion. Anthracite occurs locally in many coal-fields, such as South Wales, Scotland, and Pennsylvania. **Graphite** may represent the ultimate stage of the decomposition, since it always contains a little hydrogen.

TABLE OF ANALYSES OF COALS.

	C	H	O	N	S	Ash.	Moisture.	Coke.
1. Air-dried wood	42	5	37		—	1	15	25 charcoal
2. Air-dried peat	57·03	5·63	29·67	2·09	—	5·58	—	—
3. Lignite ...	44·93	3·12	12·51	0·64	0·50	4·43	34·28	—
Coking coals :—								
4. Northumberland	81·41	5·83	7·90	2·05	0·74	2·07	1·35	66·70
5. Wales ...	83·78	4·79	4·15	0·98	1·43	4·91	—	72·60
6. Staffordshire ...	78·57	5·29	12·88	1·84	0·39	1·03	11·29	57·21
7. Wigan Cannel ...	80·07	5·53	8·08	2·12	1·50	2·70	0·91	—
Anthracites :—								
8. South Wales ...	90·39	3·28	2·98	0·83	0·91	1·61	2·00	—
9. Pennsylvania ...	92·59	2·63	1·61	0·92	—	2·25	—	—

The total output of coal amounts to about 1000 million tons per annum. The annual outputs in Great Britain have been, in millions of tons: 1913, 287; 1916, 257; 1917, 249; 1918, 214–217. The diminishing production is a most disquieting and serious fact.

The **calorific power** of a fuel is expressed as the number of British thermal units (B.Th.U., *i.e.*, the number of lb. of water raised 1 °F. in temperature), evolved by the complete combustion of 1 lb. of the fuel, the water formed being supposed condensed to the liquid state. The following are examples: peat (30 per cent. moisture), 1462; lignite, 7065; bituminous coal, 15,000; anthracite, 15,300.

Carbides.—Compounds of metals with carbon are called **carbides.** Of the alkali metals, only lithium combines directly with carbon, forming Li_2C_2. Calcium is the only metal of the alkaline earths which unites directly with carbon, forming CaC_2; carbides of all the metals of this group are, however, produced by heating the oxides with carbon in the electric furnace: $MO + 3C = MC_2 + CO$. Beryllium is the only metal of the sub-group II which combines directly with carbon, forming BeC_2. Of the earth metals, aluminium alone unites with carbon to form Al_4C_3; the rest form carbides when their oxides are strongly heated with carbon. Iron, chromium, tungsten, and molybdenum form carbides directly, which are not attacked by water (Fe_3C, Cr_3C_2, Cr_4C, W_2C, WC, MoC, Mo_2C); manganese and uranium form Mn_3C and U_2C_3, which are decomposed by water. The remaining metals dissolve carbon but do not form carbides.

By the **action of water on carbides,** hydrocarbons, *i.e.*, compounds of carbon and hydrogen, are produced. Alkali and alkaline-earth carbides form **acetylene** C_2H_2:$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. Beryllium and aluminium carbides give **methane,** CH_4:$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$. The carbides of the rare metals, *e.g.*, thorium carbide, ThC_2, and uranium carbide, U_2C_3, form gaseous, liquid, and solid hydrocarbons; manganese carbide evolves a mixture of methane and hydrogen.

Petroleum.—Petroleum consists of liquid hydrocarbons, containing, in its natural state, dissolved gaseous and solid hydrocarbons. It is purified by agitating with concentrated sulphuric acid, and then washing with water, and is separated into fractions by distillation. The portion coming over between 40° and 150° is **petrol,** and consists chiefly of the hydrocarbons C_6H_{14}, C_7H_{16}, and C_8H_{18}. The distillate between 150° and 300° is ordinary **petroleum,** or **paraffin oil,** used for burning in lamps. The residue is **vaseline.** In some cases **paraffin wax** is contained in the residue.

Since liquid hydrocarbons similar to petroleum are formed by the action of water on metallic carbides, it has been suggested that this reaction may account for the formation of petroleum in the interior of the earth (Mendeléeff, 1877; Moissan, 1896). Another hypothesis

(Engler, 1888) is that petroleum has been formed by destructive distillation of organic remains, particularly fish.

The hydrocarbons present in paraffin oil are very inert towards chemical reagents (hence the name, from *parum affinis*). They are called **saturated hydrocarbons,** since they do not form addition compounds. The numerous members of the series have the general formula C_nH_{2n+2}, and are derived from the simplest, **methane,** CH_4, by successive addition of CH_2. A series of compounds, the successive members of which differ in composition by CH_2, is called a **homologous series.**

The cracking of oils.—The decomposition of hydrocarbons of high boiling point to simpler hydrocarbons of relatively low boiling point is effected by heating with exclusion of air, and is known as "cracking." By this process, for example, it is possible to convert heavy petroleum into petrol. A heavier residue, and gas, are at the same time produced. A catalyst, such as nickel, or chromium oxide, is used, and the reaction is carried out at 350–450°. Unsaturated hydrocarbons are also formed.

HYDROCARBONS.

Methane, or marsh gas, CH_4.—The first member of the paraffin series of hydrocarbons is **methane,** or *marsh gas*, CH_4, which is formed by the bacterial decay of vegetation (cellulose) at the bottom of marshy pools, and is liberated in bubbles when the mud is disturbed with a stick. It also occurs occluded in coal, and escapes when the pressure is relieved, forming the *fire-damp* of the mines, which, when mixed with air, causes explosions on ignition. The gas often issues in large quantities from "blowers," or fissures in the coal, and contains 80–98 per cent. of methane, with some carbon dioxide and nitrogen. *Natural gas*, from petroleum wells, contains more than 90 per cent. of methane, and is used for heating purposes instead of coal.

Methane is formed by the direct union of carbon and hydrogen on heating: $C + 2H_2 \rightleftharpoons CH_4$. By circulating hydrogen over heated sugar-charcoal more than 95 per cent. of the theoretical yield is produced. Between 1100° and 2100°, at pressures up to 200 atm., methane is the only saturated hydrocarbon formed: ethylene and acetylene are formed in smaller amounts. The percentages of methane in equilibrium with carbon and hydrogen at atmospheric pressure are: 850°, 2·5; 1000°, 1·1; 1100°, 0·6. Methane is produced when hydrogen mixed with carbon monoxide or dioxide is passed over reduced nickel at 250° or 350°, respectively:

$$CO + 3H_2 = CH_4 + H_2O.$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

In the laboratory, methane is usually prepared by heating a mixture of fused sodium acetate with three times its weight of soda-lime, in a hard glass or copper flask (Fig. 332): it is collected over water: $CH_3{\cdot}COONa + NaOH = Na_2CO_3 + CH_4$ (EXPT. 268). Prepared in this way, the gas is not very pure: it may contain up to 8 per cent. of hydrogen, and also some ethylene, C_2H_4, which causes it to burn with a slightly luminous flame.

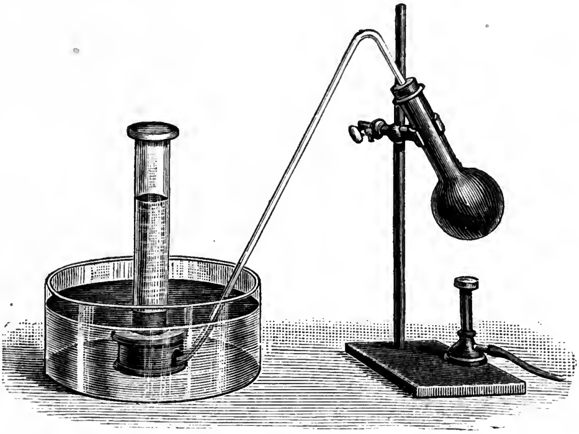


FIG. 332.—Preparation of Methane.

Pure methane is prepared by the action of water on zinc methyl, or on an ethereal solution of magnesium methyl bromide obtained by dissolving magnesium powder in a solution of methyl bromide in dry ether:

$$Zn(CH_3)_2 + 2H_2O = Zn(OH)_2 + 2CH_4.$$
$$MgCH_3Br + H_2O = Mg(OH)Br + CH_4.$$

The nearly pure gas produced by the action of water on aluminium carbide: $Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$, is purified from hydrogen by adding a little more pure oxygen than is necessary to combine with the hydrogen, and passing over palladium black. The excess of oxygen is then removed by pyrogallol, and perfectly pure methane is left.

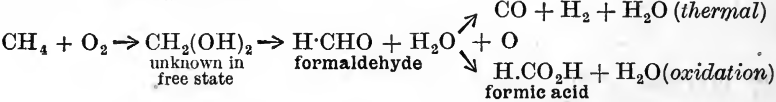
Properties of methane.—Pure methane is a colourless, odourless gas which is not poisonous. Methane is liquefied at 0° under a pressure of 140 atm., b.-pt. — 164°, m.-pt. — 184°. The critical temperature and pressure are — 82·85° and 45·6 atm. The relative density of methane is 7·97; the theoretical value is $15{\cdot}9 \div 2 = 7{\cdot}95$; hence the gas is slightly more compressible than an ideal gas. It is sparingly soluble in water: 100 vols. of water dissolve 5·5 vols. at 0°, and 3·5 vols. at 20°; but is somewhat more soluble in alcohol.

Methane is decomposed by heat directly into carbon and hydrogen: the decomposition is inappreciable at 700°, and sixty times faster at

985° than at 785°. It burns in air, or oxygen, with a pale blue non-luminous flame: $CH_4 + 2O_2 = CO_2 + 2H_2O$; its ignition point in air is 650–750°. When mixed with oxygen or air, it forms a violently explosive mixture: 1 vol. of methane requires 2 vols. of oxygen, or 9·5 vols. of air, for complete combustion. The lowest percentage of methane in air necessary for the propagation of flame is 3·75–4 by volume: the lowest ignition temperature is stated to be 500°. The composition of the gas is found by exploding a measured volume with oxygen, and measuring the volume of the residual carbon dioxide. If hydrogen is present it is first removed by adding oxygen and passing over palladium-asbestos at 100°. Hydrogen alone burns **(fractional combustion).**

By the slow combustion of methane, which occurs when a mixture of the gas with air or oxygen is passed over heated porcelain, traces of **formaledhyde,** H·COH, are formed: $CH_4 + O_2 = H{\cdot}COH + H_2O$.

According to Bone, the combustion of methane and of other hydrocarbons occurs by the entrance of oxygen into the molecule, where it is distributed between the carbon and hydrogen, giving unstable hydroxylated molecules which undergo thermal decomposition into simpler products; these, in turn, may undergo oxidation or further thermal decomposition:



$$CH_4 + O_2 \rightarrow \underset{\text{unknown in free state}}{CH_2(OH)_2} \rightarrow \underset{\textbf{formaldehyde}}{H{\cdot}CHO} + H_2O \begin{array}{l} \nearrow CO + H_2 + H_2O\ (\textit{thermal}) \\ + O \\ \searrow \underset{\textbf{formic acid}}{H.CO_2H} + H_2O(\textit{oxidation}) \end{array}$$

Dalton found (1805) that if methane is mixed with half its volume of oxygen and fired, the mixture doubles in volume, with the formation of carbon monoxide and hydrogen: $2CH_4 + O_2 = 2CO + 4H_2$. On adding a further 4 vols. of oxygen, the gas may again be fired: $2CO + 4H_2 + 4O_2 = 2CO_2 + 4H_2O$.

If 1 vol. of methane is mixed with 2 vols. of chlorine in a cylinder, and the mixture ignited by a taper, it burns with a flame, producing fumes of hydrochloric acid and a black cloud of carbon: $CH_4 + 2Cl_2 = 4HCl + C$. A mixture of equal volumes of chlorine and methane, on exposure to diffuse daylight, slowly reacts with the production of hydrogen chloride and **methyl chloride**: $CH_4 + Cl_2 = CH_3Cl + HCl$. With excess of chlorine, hydrogen is progressively replaced by chlorine until **carbon tetrachloride**, CCl_4, is formed as a final product:

1. $CH_4 + Cl_2 = HCl + CH_3Cl$, **methyl chloride.**
2. $CH_3Cl + Cl_2 = HCl + CH_2Cl_2$, **methylene chloride.**
3. $CH_2Cl_2 + Cl_2 = HCl + CHCl_3$, **chloroform.**
4. $CHCl_3 + Cl_2 = HCl + CCl_4$, **carbon tetrachloride.**

These are examples of **substitution;** 1 atom of hydrogen is displaced from the molecule and replaced by an atom of chlorine. The atom of hydrogen displaced combines with the second atom of the chlorine molecule to form a molecule of hydrogen chloride. Since methane can react only by substitution, or decomposition, not by addition, it is called a **saturated hydrocarbon.**

Ethylene, C_2H_4.—By the interaction of hydrogen and carbon at high temperatures, besides methane, traces of **ethylene,** C_2H_4, are formed, which may be absorbed by passing the cooled gas over charcoal cooled in liquid air. Most of the ethylene, however, is decomposed at the high temperature. At 1200° the ratio of methane to ethylene is 100 : 1 ; at 1400° it is 10 : 1.

Ethylene is prepared by dehydrating alcohol by means of zinc chloride, boron trioxide, phosphorus pentoxide, concentrated sulphuric acid, or syrupy phosphoric acid: $C_2H_5{\cdot}OH = C_2H_4 + H_2O$. With sulphuric acid, **ethylsulphuric acid,** $C_2H_5{\cdot}HSO_4$, is first formed and then decomposed: (1) $C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O$. (2) $C_2H_5{\cdot}HSO_4 = H_2SO_4 + C_2H_4$. This method of preparation appears to have been discovered by Becher.

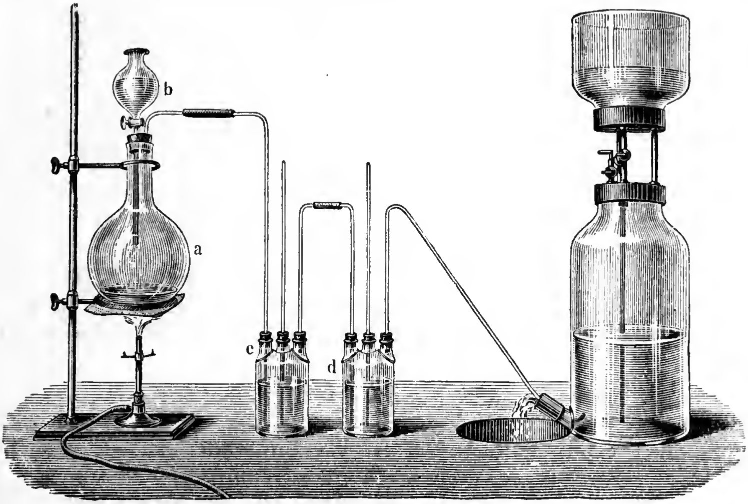


FIG. 333.—Preparation of Ethylene.

EXPT. 269.—Twenty-five gm. of alcohol and 150 gm. of concentrated sulphuric acid are heated in a 2–3 litre flask at 160–170°, and a mixture of 1 part of alcohol and 2 parts of sulphuric acid dropped in from a tap-funnel. The gas is washed with sulphuric acid to remove alcohol and ether vapour, and with caustic soda to take out sulphur dioxide. The ethylene is collected over water (Fig. 333).

Expt. 270.—According to Newth's method (1901), alcohol is dropped by a tube reaching to the bottom of a distilling flask into 50 c.c. of syrupy phosphoric acid, which has been boiled till the temperature rises to 200–220°; or alcohol vapour from one flask passed through the phosphoric acid at 220° in a second flask. The gas is passed through a tube cooled in ice. This gives a very pure gas, and is probably the best method of preparation.

Ethylene is formed from a mixture of carbon monoxide and hydrogen in contact with heated finely-divided nickel: $2CO + 4H_2 = 2H_2O + C_2H_4$.

Properties of ethylene.—Ethylene is a colourless gas with a peculiar sweet smell. It is slightly soluble in water, and very soluble in alcohol. B.-pt. − 104·3°, m.-pt. − 169°; critical temperature 9·5°, critical pressure 51 atm. On sparking the gas is decomposed into carbon and hydrogen. When passed through a red-hot tube it gives hydrogen, acetylene, and methane, with deposition of a brilliant film of amorphous carbon.

According to Bone and Coward, the thermal decomposition may be represented by the following scheme:

$$\begin{tikzcd}
 & & (a)\ C_2H_2 + H_2. \\
H_2C{:}CH_2 \arrow[r] & 2CH\vdots + H_2 \arrow[ur] \arrow[r] \arrow[dr] & (b)\ 2C + H_2 + H_2. \\
 & & (c)\ C_2H_2 + 3H_2 = 2CH_4.
\end{tikzcd}$$

The radical $CH\vdots$ is supposed to have a transient existence: it may undergo polymerisation, with formation of complex ring compounds (*cf.* p. 680).

Ethylene burns in air with a smoky, luminous flame: in oxygen the flame is very bright, and does not smoke. When mixed with oxygen in the proportions of 1 : 3 by volume and ignited, ethylene explodes violently, and undergoes complete combustion: $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$. If mixed with an equal volume of oxygen and fired by a spark, an expansion occurs, and carbon monoxide and hydrogen are formed: $C_2H_4 + O_2 = 2CO + 2H_2$. If the resulting mixture, which burns with a blue flame in air, is mixed with half its bulk of oxygen and again exploded, carbon dioxide and steam are formed: $2CO + 2H_2 + 2O_2 = 2CO_2 + 2H_2O$.

The **combustion of ethylene** is represented in Bone's scheme as follows:

$$\begin{array}{ccccccccccc}
H{\cdot}C{\cdot}H & \xrightarrow{+O_2} & H{\cdot}C{\cdot}OH & \xrightarrow{-H_2O} & H{\cdot}COH & \xrightarrow{+O_2} & H{\cdot}COOH & \xrightarrow{+O_2} & HO{\cdot}CO{\cdot}OH & \xrightarrow{-2H_2O} & CO_2 \\
\| & & \| & & & & & & & & \\
H{\cdot}C{\cdot}H & & H{\cdot}C{\cdot}OH & & H{\cdot}COH & & H{\cdot}COOH & & HO{\cdot}CO{\cdot}OH & & CO_2 \\
 & & \text{(hypothetical)} & & \textbf{2 formaldehyde} & & \textbf{2 formic acid} & & \textbf{2 carbonic acid} & & \\
 & & & & & & & & \text{(hypothetical)} & &
\end{array}$$

Hydrogen and carbon monoxide arise from the thermal decomposition of formaldehyde, as in the oxidation of methane. The liberation of free carbon in the flame is not included in this hypothetical scheme.

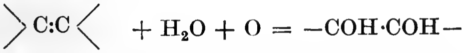
If ethylene is mixed over water with an equal volume of chlorine and the mixture exposed to light, contraction occurs and oily drops collect on the surface of the water. These consist of **ethylene dichloride,** $C_2H_4Cl_2$, or *Dutch liquid*, formed by the direct addition of chlorine to the double bond in the ethylene molecule:

$$H_2C{:}CH_2(\rightarrow H_2\cdot\overset{|}{C}\cdot\overset{|}{C}H_2) + Cl_2 = CH_2Cl\cdot CH_2Cl.$$

On account of this reaction, ethylene was first called **olefiant gas** (*i.e.*, oil-forming gas) by Fourcroy. Ethylene dichloride was discovered by the Dutch chemists, Deimann and Paets van Troostwyck, in 1781. If passed into bromine covered with a layer of water, ethylene combines with the halogen to form a colourless, pleasant-smelling liquid, **ethylene dibromide,** $C_2H_4Br_2$, or $CH_2Br\cdot CH_2Br$, similar to the dichloride.

A mixture of 1 vol. of ethylene and 2 vols. of chlorine, when ignited, burns with a red flame, fumes of hydrochloric acid and a dense black cloud of soot being formed: $C_2H_4 + 2Cl_2 = 4HCl + 2C$.

Ethylene forms additive compounds with iodine, hydrobromic acid, and hydriodic acid at 100°, but not with hydrochloric acid: $CH_2{:}CH_2 + HBr = CH_3\cdot CH_2Br$. When mixed with hydrogen and passed over reduced nickel at 130–150°, it forms the saturated hydrocarbon **ethane**: $C_2H_4 + H_2 = C_2H_6$, or $CH_2{:}CH_2 + H_2 = CH_3\cdot CH_3$. Hypochlorous acid forms **glycol chlorohydrin**: $CH_2{:}CH_2 + HOCl = CH_2\cdot OH\cdot CH_2Cl$. Cold dilute potassium permanganate solution is decolorised by ethylene, hydrated manganese dioxide is deposited, and the ethylene is oxidised to **glycol**: $CH_2 : CH_2 + H_2O + O = \begin{array}{l}CH_2\cdot OH\\ | \\ CH_2\cdot OH.\end{array}$ This reaction with potassium permanganate is characteristic of a double bond between carbon atoms:



$$>C{:}C< \; + H_2O + O = -COH\cdot COH-$$

Concentrated sulphuric acid absorbs ethylene, slowly on shaking at the ordinary temperature, rapidly at 160–170°, with the formation of **ethylsulphuric acid,** or **sulphovinic acid,** $C_2H_5\cdot HSO_4$: $C_2H_4 + H\cdot HSO_4 = C_2H_5\cdot HSO_4$. When this is boiled with water, **alcohol** is produced: $C_2H_5\cdot HSO_4 + HOH = C_2H_5\cdot OH + H_2SO_4$. Fuming sulphuric acid rapidly absorbs ethylene, a reaction used in gas analysis as an alternative to absorption by bromine water, for the estimation of ethylene. **Ethionic acid,** $C_2H_4\cdot H_2S_2O_7$, and **carbyl sulphate,** $C_2H_4S_2O_6$, are formed.

Acetylene, C_2H_2.—By the action of water on the carbide of potassium formed in the preparation of the metal from potassium carbonate and charcoal, Edmund Davy (1836) obtained a new hydrocarbon, which was rediscovered by Berthelot in 1859, and called by him **acetylene.** He showed that it is formed when ethylene or alcohol vapour is passed through a red-hot tube, but an important fact discovered in this work was the formation of acetylene by **direct synthesis** from its elements, when an electric arc burns between carbon poles in an atmosphere of hydrogen (Fig. 334): $2C + H_2 \rightleftarrows C_2H_2$. Small quantities of methane and ethane are also formed, apparently by independent reactions.

FIG. 334.—Berthelot's Synthesis of Acetylene.

Acetylene is produced when a Bunsen burner "strikes back," *i.e.*, when the coal gas burns at the lower small jet, with a limited supply of air and in contact with the metal tube, which cools the flame. The peculiar smell noticed is usually said to be due to the presence of acetylene; although this odour always accompanies the formation of acetylene in the reaction, it appears to be due to some other substance. The acetylene probably arises from the thermal decomposition of the ethylene in the coal gas.

EXPT. 271.—The presence of acetylene in the gas issuing from the burner is readily detected by holding over it a large globe wetted inside with an ammoniacal solution of cuprous chloride (p. 816). The dark blue liquid rapidly becomes covered with a red film, owing to the precipitation of **cuprous acetylide,** Cu_2C_2, an explosive substance.

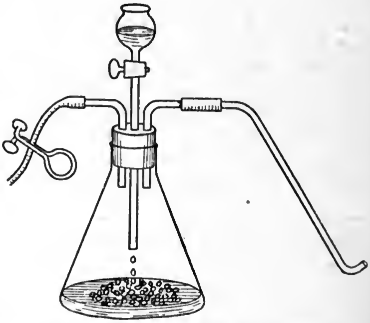


FIG. 335.—Preparation of Acetylene.

Acetylene is prepared for use in illumination by the action of water on **calcium carbide**: $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$.

EXPT. 272.—Cover the bottom of a conical flask with a layer of sand, and place on this a small heap of granular calcium carbide. Fit the flask with a rubber stopper carrying a dropping funnel, and inlet and outlet tubes for gas (Fig. 335). Displace the air with a current of coal gas, and then allow water to drop slowly on the carbide. Acetylene is rapidly evolved, and will burn at the end of the exit tube with a very luminous, smoky flame. The acetylene prepared from commercial carbide has an unpleasant smell, due to the presence of impurities, such as phosphine, PH_3. These may be removed by passing through a solution of bleaching powder.

Acetylene generators, used for the preparation of the gas, act either on the principle of the Kipp's apparatus (p. 185), or else a regulated stream of water is allowed to drop on the carbide.

Acetylene is formed when ethylene dibromide is dropped into boiling alcoholic potash. The bromine is removed together with hydrogen, in the form of two molecules of hydrobromic acid: $CH_2Br{\cdot}CH_2Br = C{:}HCH + 2HBr$. The compound C_2H_3Br is formed in an intermediate stage.

Properties of acetylene.—Acetylene is a colourless gas which is said to have an ethereal smell when pure, but ordinarily has an unpleasant odour. When strongly cooled it forms a white solid, subliming at − 85°. Under 1·25 atm. pressure the solid melts at − 81° to a colourless liquid. The critical temperature of acetylene is 35·5°; the critical pressure is 61·5 atm. The gas dissolves in its own volume of water, and is very soluble in alcohol. Acetylene ignites at 480° in air, burning with a very smoky, luminous flame, but if it is supplied to special burners under a pressure of 2–8 in. of water, so as to escape through fine capillaries and mix with a regulated amount of air, the flame is very bright and does not smoke. Acetylene explodes with oxygen with extreme violence: it is unsafe to try the experiment with ordinary precautions, as strong glass vessels are shattered by the explosion.

Mixtures of acetylene and air, in proportions varying from 4 : 5 to 4 : 80, are explosive. Coal gas is only explosive when mixed with air within the limits 1 of gas to 5–13 of air, and the lower limit of explosion for methane is 5·3 per cent. in air. The danger of explosion from escape of acetylene is therefore much greater than with coal gas.

Acetylene is less poisonous than carbon monoxide, or even than coal gas (which contains the latter); it forms with the hæmoglobin of the blood a compound which, unlike that produced by carbon monoxide, is unstable, and is readily decomposed by aeration.

Acetylene is formed from its elements with considerable absorption of heat: $2C + H_2 = C_2H_2 - 47{\cdot}8$ kgm. cal. It is for this reason unstable, and readily explodes under moderate pressure. The gas is therefore generated only as required, or is absorbed in acetone, which dissolves 300 vols. of the gas under 12 atm. pressure. The acetone is soaked up in porous material ("kapok"), contained in a steel bottle (p. 189). The chief use of acetylene is for illumination, and for the oxy-acetylene blowpipe.

The unsaturated character of acetylene is shown by its capacity of forming **addition compounds.** Chlorine combines violently with the gas, forming the dichloride, $CHCl{:}CHCl$, and the tetrachloride, $CHCl_2{\cdot}CHCl_2$. Under the influence of platinum black, acetylene combines with two or four atoms of hydrogen, forming ethylene or ethane, C_2H_4 or C_2H_6, respectively. Hydrobromic acid forms $CH_2{:}CHBr$, and $CH_3{\cdot}CHBr_2$ (ethylidene bromide, isomeric with ethylene dibromide, $CH_2Br{\cdot}CH_2Br$).

If acetylene is passed into a boiling solution of 3 vols. of sulphuric acid and 7 vols. of water to which a few per cent. of mercuric sulphate is added, **acetaldehyde,** $CH_3{\cdot}CHO$, is continuously formed and distils off. The first reaction is the formation of a mercury compound which is decomposed by the acid. With mercuric chloride solution, a white precipitate of the compound, **trichloromercuriacetaldehyde,** $(ClHg)_3C{\cdot}CHO$, is formed, which is hydrolysed by acids to acetaldehyde. Another compound, $HgCl_2,C_2H_2$, is also formed in alcoholic solution. The addition of water to acetylene, with formation of acetaldehyde, which occurs in the reactions:

$$2C_2H_2 + 2H_2O + 6HgCl_2 = 2(ClHg)_3C{\cdot}CHO + 6HCl\,;$$
$$2(ClHg)_3C{\cdot}CHO + 6HCl = 2CH_3{\cdot}CHO + 6HgCl_2,$$

is the basis of an important technical process. From acetaldehyde, by reduction with hydrogen, **alcohol,** $CH_3{\cdot}CH_2{\cdot}OH$, can be obtained; on oxidation, aldehyde yields **acetic acid,** $CH_3{\cdot}COOH$; both are important materials. The use of alcohol, alone or mixed with benzene, as a fuel in motor engines instead of petrol, is now an accomplished fact, and the cheap production of calcium carbide is also possible where power from water is available. It is not certain, however, that it may not be cheaper to obtain alcohol by fermentation.

When acetylene is heated to dull redness, a complicated polymerisation reaction occurs, and a liquid mixture of hydrocarbons is obtained, one of which is **benzene**: $3C_2H_2 = C_6H_6$. This is an example of the conversion of an aliphatic into an aromatic hydrocarbon. A certain amount of the acetylene appears also to break up into the free radicals, $CH\vdots$, which decompose into carbon and hydrogen, the latter combining with the $CH\vdots$ to form methane, CH_4.

Coal gas.—The destructive distillation of coal, with the formation of gas, was first carried out by the Rev. John Clayton in 1688, the results being published in 1739. It was also described by Bishop Watson, who found that a permanent gas, tar, and a watery liquid were formed. The use of coal gas as an illuminant was introduced by William Murdoch in 1792; in 1798 he installed a gas plant for lighting the factory of Boulton and Watt, at Soho, near Birmingham. Gas lighting was introduced into Manchester factories in 1808, the first public gas-works being erected at Salford, and about the same time gas lighting was used, on a very small scale, in London. The capital was lighted by gas in 1812, Paris following in 1815, but the use of gas in dwelling-houses came much later.

In the gas-works bituminous coal, alone or mixed with cannel, is heated in fireclay **retorts,** *A* (Fig. 336), which may be horizontal, inclined, or vertical. These are heated by producer gas (p. 705), formed by passing air and steam through incandescent coke resting on bars in a firebrick well beneath each retort, the gas formed being burnt under the latter. The gas evolved from the coal in the retorts passes, by way of vertical ascension pipes, to a common **hydraulic main,** *B*, consisting of a long horizontal iron cylinder into which these pipes lead. The main serves as

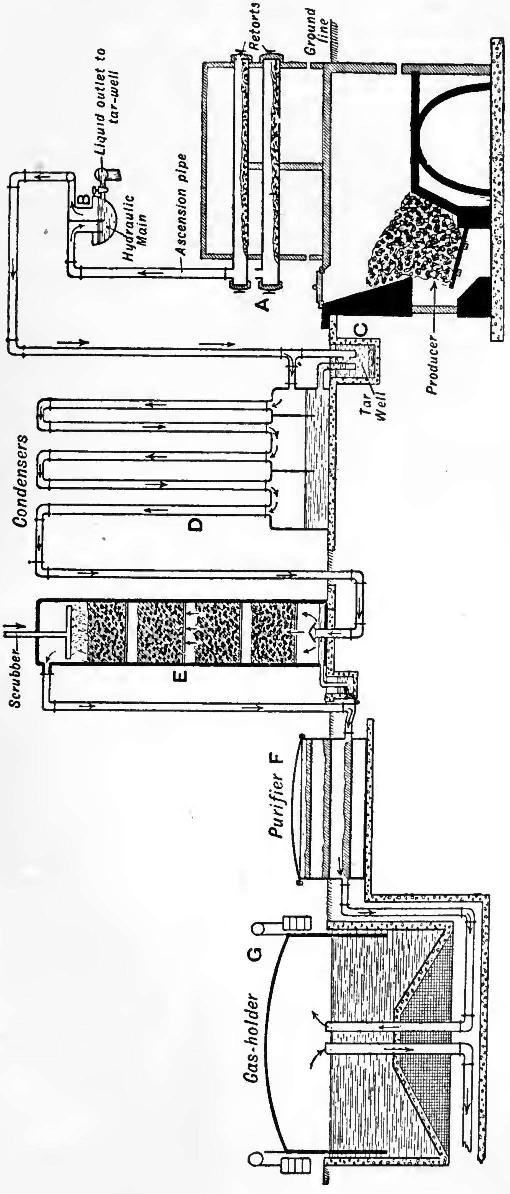


FIG. 336.—Coal-gas Manufacture.

a water-seal, preventing gas passing back when a retort is opened.

In the hydraulic main separation occurs into **crude gas, ammoniacal liquor,** and **tar.** The gas leaving the main, at 50–60°, contains the following impurities, which must be removed :

Ammonia,	0·7 — 1·4	per cent. by volume.
Hydrocyanic acid,	0·05 — 0·15	,, ,, ,,
Sulphuretted hydrogen,	0·9 — 1·7	,, ,, ,,
Carbon disulphide,	0·02 — 0·04	,, ,, ,,

More tar is separated in the **condensers,** *D*, consisting of a series of vertical iron cooling pipes. Ammoniacal liquor is deposited with the tar, and the two collect in the **tar-well,** *C*. The gas next passes to a special **tar separator,** and is drawn by an **exhauster** to the **scrubbers,** *E*. These are iron towers packed with coke, down which water passes. The rest of the ammonia is thus removed.

The gas passing from the scrubbers contains as impurities carbon dioxide, some sulphuretted hydrogen (a portion of each gas is deposited with the ammonia in the previous cooling and scrubbing), and carbon disulphide. A cubic foot of crude gas usually contains 800 grains of sulphur as H_2S and 40 grains as CS_2. These impurities are removed by the **purifiers,** *F*, in which the gas passes over trays covered with slaked lime, or hydrated ferric oxide. The lime absorbs sulphuretted hydrogen, forming calcium hydrosulphide : $Ca(OH)_2 + 2H_2S = Ca(SH)_2 + 2H_2O$. The oxide of iron decomposes the sulphuretted hydrogen with formation of ferric sulphide, Fe_2S_3, or a mixture of ferrous sulphide and sulphur : $Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$. The oxide is "revived" by exposure to air, when sulphur is separated, and hydrated ferric oxide regenerated : $2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S$. When it contains 50 per cent. of sulphur, the "spent oxide" is burnt to produce sulphuric acid (p. 503). The old method of removing carbon disulphide was to pass the gas through lime previously used to remove sulphuretted hydrogen ("foul lime"), when a thiocarbonate is formed : $Ca(SH)_2 + CS_2 = CaCS_3 + H_2S$. The sulphuretted hydrogen evolved is removed in a second oxide purifier. Usually the carbon disulphide is left in the gas, or removed by a catalytic process, in which the gas is passed over nickel at 450° : $CS_2 + 2H_2 = 2H_2S + C$. The sulphuretted hydrogen is removed as usual.

The purified gas is now passed to the **gas-holder,** *G*, a counterpoised iron bell sealed below by water. From this it is distributed to the mains. The purified gas should contain less than 1 part of H_2S per 10,000,000 parts, *i.e.*, it should not blacken lead acetate paper.

Cyanides, which are of value, are removed from the crude gas by passing through ammoniacal liquor containing ammonium sulphide, with powdered sulphur in suspension. A solution of **ammonium thiocyanate** is formed: $(NH_4)_2S_2 + NH_4CN = (NH_4)_2S + NH_4CNS$.

The average **composition** of genuine coal gas, in percentages by volume, is as follows:

Hydrogen,	43 — 55	"**Diluents,**" non-illuminating, but heat-producing.
Methane,	25 — 35	
Carbon monoxide,	4 — 11	
Olefines, acetylene and benzene	2·5 — 5	**Illuminants.**
Nitrogen (from air leakage)	2 — 12	**Impurities.**
Carbon dioxide	0 — 3	
Oxygen	0 — 1·5	

The **calorific power** of good coal gas is about 16,000 B.Th.U. per lb. or 600 B.Th.U. per cu. ft.

The hydrogen is derived from the thermal decomposition, at 700–800°, of gaseous hydrocarbons in contact with the hot walls of the retort. The carbon formed is deposited as a hard greyish-black mass of **gas carbon,** which is removed by chipping. This is a very pure form of amorphous carbon, of density 2·35, which is a good conductor of electricity, and is used for the pencils of arc lamps or in electric batteries.

The luminosity of genuine coal gas flames is due entirely to the 5 per cent. of olefine hydrocarbons, acetylene (0·06–0·07 per cent.), and benzene vapour.

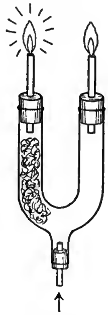


FIG. 337.—Luminosity imparted to Hydrogen Flame by Benzene Vapour.

EXPT. 273.—The effect of such hydrocarbons on the luminosity of flames may be illustrated by fitting a hard glass jet to each arm of a **Y**-tube, in one arm of which is a piece of cotton-wool soaked in benzene (Fig. 337), attaching the tube to a hydrogen apparatus, and lighting the two jets. The hydrogen saturated with benzene vapour burns with a luminous flame.

Modern coal gas is usually mixed with water gas (p. 705), produced by blowing steam over the red-hot coke in the retorts: $C + H_2O \rightleftarrows CO + H_2$. In this way the percentage of carbon monoxide is increased, and that of methane diminished. Owing to leakage of air, the nitrogen content often exceeds 20 per cent. The quality of the resulting gas is consequently mediocre as compared with the old genuine coal gas, or coke-oven gas, and this has led to a very natural prejudice against gas for domestic fires.

Coke.—The red-hot residue in the gas retorts is raked out, or pushed out by rams, through doors opened at the front and back, and is quenched with water. It is known as **gas coke,** and is used as fuel. It is greyish-black, porous, and brittle, and contains all the ash of the coal, most of the sulphur, and small quantities of nitrogen, hydrogen, and oxygen. The average percentage of carbon is 81, hence coke is usually classed as a variety of amorphous carbon.

	C	H	O	N	S	Ash	H_2O
Coal:	58·44	3·75	5·99	1·08	1·92	10·05	18·77
Coke:	75·1	0·49	2·39	0·58	2·63	19·77	—

The yields from 1 ton of Newcastle coal, in gas-making, are: 12,500 cu. ft. of gas; 110 lb. of tar, yielding 77 lb. of pitch; 7lb. of ammonia, and 65–70 per cent. of the weight of the coal is left as coke.

A hard variety of coke for metallurgical purposes (*e.g.*, blast furnaces) is prepared by carbonising coal in **coke-ovens.** The old "beehive" oven consists of a covered mound of brickwork, in which the coal is partly burnt in a limited supply of air, as in charcoal burning. The high temperature produced carbonises the rest of the coal, and all the volatile products are lost. In modern "recovery ovens," *e.g.*, the Otto or Simon-Carvès ovens, the coal is heated in closed fireclay retorts, *O*, 24 ft. long and 2 ft. wide, by flues, *T*, passing between them in which part of the gas evolved, mixed with preheated air, is burnt. The gas from the ovens (Fig. 338) is cooled to separate tar, scrubbed to remove ammonia, and part is burnt in the flues. The coke is pushed out by rams, and quenched. On account of the value of the tar, benzene, and ammonia, the use of recovery ovens is rapidly replacing the wasteful "beehives."

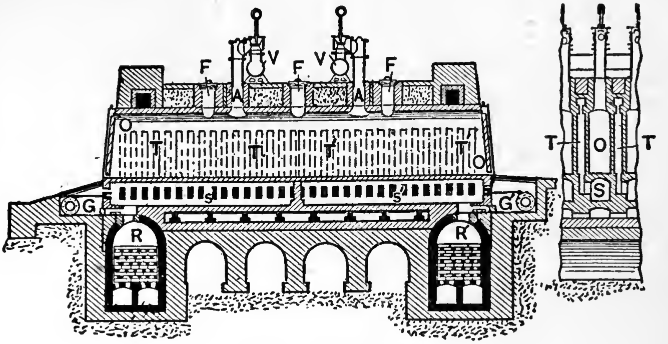


FIG. 338.—Coke-ovens.

If powdered coke is mixed with pitch or tar-oil, moulded, and strongly heated in closed retorts, a compact variety of amorphous carbon, which is a good conductor of electricity, is obtained. This process is used in the manufacture of **carbon electrodes** for electric furnaces.

EXERCISES ON CHAPTER XXXIII

1. Give a concise account of the properties of the two crystalline forms of carbon. How may graphite be obtained from amorphous carbon ?

2. How would you determine whether a given specimen of carbon was (*a*) graphite, (*b*) diamond, (*c*) amorphous carbon ? How is graphite purified, and for what purposes is it used ?

3. What method was used to convert charcoal into diamonds ? What is supposed to be the condition under which transformation occurs ?

4. What are the modifications of amorphous carbon ? How are they made, and for what purposes are they used ?

5. Describe experiments illustrating the property of charcoal of absorbing gases and dissolved substances. What general connection is there between the properties of a gas and the extent to which it is absorbed by charcoal ?

6. How has coal been produced ? What common varieties of coal are recognised, and what differences are there in their chemical compositions ?

7. How are carbides prepared, and what is the action of water on these substances ?

8. What are saturated and unsaturated hydrocarbons ? Describe the preparation and properties of one typical member of each of these groups.

9. What reactions are supposed to take place in the combustions of hydrocarbons ? How may a mixture of hydrogen and methane be analysed by the method of fractional combustion ?

10. How are (*a*) ethylene, (*b*) acetylene, prepared ? What is the action of concentrated sulphuric acid on these substances ? How may they be converted into alcohol ?

11. What is meant by substitution ? How are the facts of substitution at variance with the electrochemical theory of Berzelius ?

12. How is coal gas manufactured and purified ? What is the composition of genuine coal gas ?

13. What is coke ? How is it made on the large scale, and for what purposes is it used ?

14. What is the calorific power of a fuel ?

15. Forty c.c. of a mixture of hydrogen, methane, and nitrogen were exploded with 10 c.c. of oxygen. After cooling, the residual gas measured 36·5 c.c. On treatment with caustic potash the volume diminished to 33·5 c.c., and on treatment with alkaline pyrogallol to 32 c.c. Calculate the percentage composition of the original mixture.

16. Calculate from the following data the composition of a mixture of methane, ethane, and hydrogen : vol. of gas taken, 53·5 c.c. ; vol. of oxygen added, 250 c.c. ; vol. after explosion, 194·95 c.c. ; residue after treatment with potash, 138·35 c.c.

CHAPTER XXXIV

OXYGEN COMPOUNDS OF CARBON, ETC.

The oxides of carbon.—Three **oxides of carbon,** all gaseous at the ordinary temperature, are definitely known:

Carbon dioxide, or **carbonic anhydride,** CO_2, the anhydride of the hypothetical **carbonic acid,** H_2CO_3.

Carbon monoxide, or **carbonic oxide,** CO, the anhydride of **formic acid,** H_2CO_2.

Carbon suboxide, C_3O_2, the anhydride of **malonic acid,** $C_3H_4O_4$.

The oxides C_4O_3, C_8O_3, and $C_{12}O_9$ have been described, but their existence is doubtful. The monoxide and dioxide are the only oxides of carbon of practical importance.

CARBON DIOXIDE, CO_2.

Carbon dioxide, CO_2.—This gas, first prepared by Van Helmont in 1630 (p. 30), examined by Joseph Black in 1755 (p. 35), and more fully by Bergman (1774), was clearly recognised as an oxide of carbon by Lavoisier in 1785. Lavoisier determined its composition by burning charcoal and the diamond in oxygen, showed that it combines with bases to form salts, as had been discovered by Black, and called it *acide carbonique.* It was long known as **carbonic acid gas.**

Carbon dioxide issues in abundance from the earth in certain localities, such as the Valley of Death (Java) and the Grotto del Cane (Naples). It occurs in many mineral waters, such as those of Selters, Vichy, and the Geyser Spring of Saratoga. By the combustion of coal and other carbonaceous fuels, large quantities of carbon dioxide pass into the atmosphere. The latter contains about 3 vols. of CO_2 in 10,000. Carbon dioxide is formed during *respiration,* as may be shown by blowing expired air through lime-water, which becomes turbid. The *fermentation* of sugar, in the preparation of beer and wine, produces carbon dioxide and alcohol: $C_6H_{12}O_6 = 2C_2H_5{\cdot}OH$ (*alcohol*) $+ 2CO_2$. Other kinds of fermentation and the decay of organic matter also produce carbon dioxide.

EXPT. 274.—Dissolve 10 gm. of glucose in 250 c.c. of warm water, in a flask fitted with a tube dipping into lime-water (Fig. 339). When the temperature falls to 30° add a little yeast, and allow the apparatus to stand for a day or two. The contents effervesce, and bubbles of gas pass through the lime-water, rendering it milky. The liquid may be distilled (p. 93), when weak alcohol passes over.

Large quantities of carbon dioxide produced by fermentation in breweries are collected and liquefied by compression. The liquid is sold in large steel cylinders, from which the gas may be taken by standing the cylinder upright with the valve above. If the cylinder is laid on its side, and the valve opened, a jet of liquid carbon dioxide issues from it, which, owing to further cooling by rapid evaporation, at once freezes to a snow-like **solid.** The latter may be collected by firmly tying a canvas bag to the jet, and intermittently opening the latter fairly widely. The solid may be handled with a horn spoon; if pressed between the fingers it produces painful blisters.

The boiling point of carbon dioxide is − 56° under 5·3 atm. pressure. The sublimation point of the solid at atmospheric pressure is − 78·2°; this temperature is attained in a mixture of solid carbon dioxide and ether, which is a convenient cooling agent in the laboratory, and may be contained in a Dewar flask. A second form of the solid appears to exist under high pressure. The liquid cannot exist under atmospheric pressure.

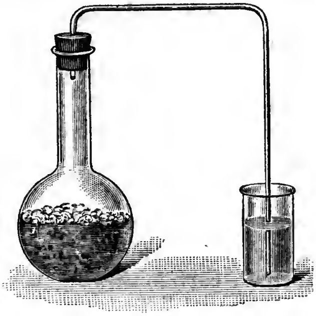


FIG. 339.—Carbon Dioxide by Fermentation.

EXPT. 275.—Cut a circular groove in a piece of board, and fill it with mercury. Place over the whole a mixture of solid carbon dioxide and ether, by means of a horn spoon. The mercury rapidly freezes. Knock out the ring of solid mercury, and suspend it by a glass hook in a jar of water. A thick ring of ice is formed, and the mercury melts.

If solid carbon dioxide is sealed up in a strong glass tube, it melts under pressure to a liquid. If the tube is warmed gently, the liquid expands very rapidly, until at 31° the meniscus disappears. At the same instant the tube is filled with a flickering fog, which at once vanishes. On cooling the reverse changes occur: 31° is the **critical temperature** of carbon dioxide; the critical pressure is 72·85 atm. (p. 170).

Preparation of carbon dioxide.—Carbon dioxide is prepared in the laboratory by the action of acids on carbonates. The very unstable **carbonic acid,** H_2CO_3, is probably an intermediate product: $2H^{\cdot} + CO_3'' \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2 + H_2O$.

EXPT. 276.—Pieces of marble and dilute hydrochloric acid, in a Woulfe's bottle or Kipp's apparatus, are generally used for the preparation of carbon dioxide: $CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$. The gas is washed with a little water, or passed through a solution of sodium bicarbonate, to eliminate acid spray, and is then collected by downward displacement, since it is 1·53 times as heavy as air. If required free from air, the gas is collected over mercury.

If *dilute* sulphuric acid is added to marble, the latter soon becomes coated with sparingly soluble calcium sulphate, $CaSO_4,2H_2O$, and the action ceases. If finely-powdered chalk is used instead of marble, the reaction is complete, but frothing occurs. Marble or chalk dissolves readily in concentrated sulphuric acid if a little water is added, since the calcium sulphate forms a soluble acid sulphate, $CaH_2(SO_4)_2$. To remove sulphur dioxide, which is a common impurity, the gas is passed through potassium permanganate solution.

Pure carbon dioxide is obtained by heating pure sodium bicarbonate: $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$; by the action of dilute sulphuric acid on pure sodium carbonate:

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O;$$

or by heating a mixture of 1 part of sodium carbonate with 3 parts of potassium dichromate.

Carbon dioxide is evolved on heating all carbonates except the normal carbonates of the alkali metals and barium carbonate. *E.g.*, chalk, limestone, marble, *magnesia alba*, etc., give off carbon dioxide at a red heat: $CaCO_3 \rightleftharpoons CaO + CO_2$. The gas is therefore produced in lime-burning (p. 841).

An impure gas, mixed with nitrogen, is formed by passing a slight excess of air over red-hot coke or charcoal: $C + O_2 = CO_2$. If this gas is passed into a concentrated solution of potassium carbonate, the carbon dioxide is absorbed, with production of bicarbonate. On heating the solution, the carbon dioxide is expelled, free from nitrogen, leaving a solution of potassium carbonate, which is used over again: $K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3$.

Baking-powder contains sodium bicarbonate and tartaric acid, which do not react when dry. In presence of water, carbon dioxide is evolved, the bubbles of which are expanded by heat on baking:

$$2NaHCO_3 + C_4H_6O_6 \ (\textit{tartaric acid}) = Na_2C_4H_4O_6 + 2CO_2 + 2H_2O.$$

Health salt is a similar mixture. The fermentation produced by yeast in the baking of bread forms carbon dioxide, which gives the dough a spongy texture.

Properties of carbon dioxide.—Carbon dioxide is a colourless gas with a faint pungent smell and an acid taste. It extinguishes a burning taper, sulphur, phosphorus, etc.; air containing 2½ per cent. by volume of carbon dioxide will not support the combustion of a taper, although 18½ per cent. of oxygen is still present. The gas is therefore used in extinguishing fires.

Expt. 277.—Ignite a little benzene in a porcelain dish, and decant over it a large bell-jar of carbon dioxide. The flame is extinguished.

Fire extinguishers consist of a strong metal vessel containing a solution of sodium carbonate, with a glass tube of sulphuric acid inside. By means of a rod attached to a knob outside, the glass tube may be broken, and the mixture of liquid and gas then issues forcibly from the nozzle.

Carbon dioxide does not support respiration; animals die in it from suffocation, but the gas is not poisonous, and if oxygen is taken in time recovery with no ill-effects follows.

Burning sodium, potassium, and magnesium continue to burn in carbon dioxide, with separation of pure carbon: $CO_2 + 2Mg = 2MgO + C$.

Expt. 278.—Burn a piece of magnesium ribbon in a jar of dry carbon dioxide. Treat the residue with dilute sulphuric acid; magnesia dissolves, and black specks of carbon are seen floating in the liquid.

A mixture of solid carbon dioxide and magnesium powder burns with a brilliant flash when ignited, leaving magnesia and carbon.

A characteristic reaction of carbon dioxide is the formation of a white precipitate of calcium or barium carbonate when the gas is passed through, or shaken with, lime- or baryta-water. The calcium carbonate dissolves in excess of carbon dioxide, but barium carbonate is insoluble (p. 206). Sulphur dioxide also gives a white precipitate (calcium sulphite, $CaSO_3$) with lime-water, but is absorbed by potassium permanganate solution.

Carbon dioxide is fairly soluble in water (p. 97); the latter, at 15°, dissolves about its own volume of the gas. Under pressures greater than 4–5 atm., at the ordinary temperature, the solubility increases at a slower rate than the pressure (*i.e.*, according to Henry's law). On lowering the pressure, the gas escapes with vigorous effervescence, although the liquid remains supersaturated, and evolves gas slowly for some time. If the liquid is stirred, or if porous solids such as sugar or bread-crumbs are thrown into it, brisk effervescence results. The whole of the carbon dioxide dissolved in water is expelled on boiling.

Aerated waters (*e.g.*, *soda-water*) are charged with carbon dioxide under pressure; "sparklets" are small iron bulbs containing liquid carbon dioxide.

Carbonic acid.—The aqueous solution of carbon dioxide has a faintly acid taste, and turns litmus a port wine red colour. If the amount of dissolved gas is increased by pressure, the litmus turns bright red. On boiling, carbon dioxide escapes, and the blue colour is restored.

A portion of dissolved gas appears to be combined with water to form **carbonic acid,** H_2CO_3, and the solution shows very feebly acidic properties. It appears to be only about one-fifth the strength of acetic acid; the latter displaces carbon dioxide from carbonates. Carbonic acid obeys Ostwald's dilution law, and the dissociation constants have been given as:

$$\begin{aligned}[H^{\cdot}] \times [HCO_3''] / [H_2CO_3] &= 3{\cdot}04 \times 10^{-7} \text{ at } 18^\circ; \\ [H^{\cdot}] \times [CO_3''] / [HCO_3'] &= 6 \quad\ \times 10^{-11} \text{ at } 25^\circ.\end{aligned}$$

From theoretical considerations one would expect carbonic acid to be stronger than formic acid, $H{\cdot}CO{\cdot}OH$, since the addition of a hydroxyl group, forming $HO{\cdot}CO{\cdot}OH$, should increase the acidic properties. It is found that the neutralisation of carbonic acid by alkali, with phenolphthalein as indicator, is not instantaneous, as is the case in ionic reactions, so that it is assumed that less than 1 per cent. of the carbon dioxide is hydrated. The hydration reaction: $CO_2 + H_2O \rightleftharpoons H_2CO_3$, requires time. If the hydrogen ions in the solution are referred, not to the total CO_2, as above, but to the hydrated part, H_2CO_3, carbonic acid is found to be twice as strong as formic acid.

Carbon dioxide is more soluble in alcohol than in water. Since it dissociates in two stages, it is a **dibasic acid** and forms two series of salts:

1. **Acid carbonates,** *e.g.*, $NaHCO_3$, $Ca(HCO_3)_2$;
2. **Normal carbonates,** *e.g.*, Na_2CO_3, $CaCO_3$.

The structural formula of the acid is written $HO{\cdot}CO{\cdot}OH$; esters of the hypothetical **orthocarbonic acid,** $C(OH)_4$, *e.g.*, ethyl orthocarbonate, $C(OC_2H_5)_4$, are known. The acid H_2CO_3 is **metacarbonic acid.** A crystalline hydrate, $CO_2,6H_2O$, is obtained under pressure at low temperatures.

The normal carbonates of alkali metals are hydrolysed in solution, and exhibit an alkaline reaction: $Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3$. A decinormal solution of sodium carbonate is 3·17 per cent. hydrolysed at 25°.

Dissociation of carbon dioxide.—At high temperatures, carbon dioxide is slightly dissociated into carbon monoxide and oxygen: $2CO_2 \rightleftharpoons 2CO + O_2$: the number of molecules dissociated per 100 molecules of CO_2 at different temperatures at atmospheric pressure is shown below (*cf.* dissociation of steam, p. 212):

Temperature :	1027°	1170°	1227°	1292°	2367°	2672°	2743°
Percentage dissociation :	0·004	0·025	0·04	0·06	21·0	65	76

Deville (1865) found that if a rapid stream of carbon dioxide was passed through a porcelain tube heated to about 1300°, and the issuing gas collected over potash, a small amount of a mixture of carbon monoxide and oxygen was obtained, indicating a dissociation of about 0·2 per cent. The gas is also decomposed by electric sparks, or the silent discharge; at 3–5 mm. pressure 65–70 per cent. is decomposed by the silent discharge.

The composition of carbon dioxide.—The **composition of carbon dioxide** may be found directly both by weight and by volume. The **composition by weight** is determined by burning a weighed amount of pure carbon in oxygen, and weighing the carbon dioxide, usually after absorption.

Expt. 279.—Weigh about 1 gm. of purified sugar-charcoal into a porcelain boat. Place the boat, *X*, inside a hard glass tube, *Y*, one half of which is packed with recently-ignited granular copper oxide, *Z* (Fig. 340). By means of rubber stoppers fit the tube to the purifying apparatus consisting of U-tubes *A* and *B*, containing broken sticks of caustic potash, and the absorption apparatus, consisting of the weighed **potash-bulbs**, *C*, containing a concentrated solution of caustic potash, with a calcium chloride tube, *D*, attached. During weighing, these are closed by bits of glass rod and rubber tubing. Lay the tube in an iron tray, lined inside with asbestos, in a combustion furnace. Sheets of asbestos are placed over the ends of the tube, to protect the rubber stoppers from heat radiated from the furnace. The burners underneath the copper oxide are lighted, and the latter is heated to redness, a *slow* stream of oxygen from a gas-holder being passed through the apparatus. The burners under the boat are now lighted, and the combustion of the carbon is carried out. The layer of hot copper oxide oxidises any carbon monoxide which may be formed to carbon dioxide. Allow the oxygen to pass for a few minutes after the combustion is finished, to sweep out all the carbon dioxide, then pass air through to displace the oxygen. Detach the potash-bulbs, closing them with the pieces of glass rod and rubber tubing as in the previous weighing, cool and reweigh. The increase in weight represents the carbon dioxide formed. Let x = wt. of carbon, y = wt. of carbon dioxide; then $y - x$ = wt. of oxygen. $\therefore$ *carbon/oxygen* in carbon dioxide $= x/(y - x)$.

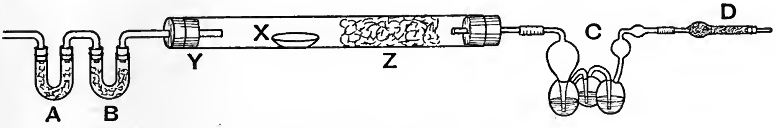


Fig. 340.—Gravimetric Composition of Carbon Dioxide.

Dumas and Stas (1841) carried out in this way five combustions of natural graphite, four of artificial graphite, and five of diamond. The results were in agreement, the mean values being as follows :

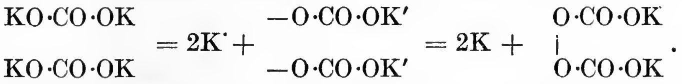
800 parts of oxygen combine with :
299·94 parts of natural graphite,
299·95 parts of artificial graphite,
300·02 parts of diamond.

Due allowance was made for ash remaining in the boat after the combustion. The mean value of the **equivalent of carbon** $(O = 8)$ was taken as 2·9994 ; this was corrected by Scott for the expansion of the potash solution after it has absorbed carbon dioxide, which makes a slight difference to the buoyancy correction in the weighings, and reduces the equivalent to 2·9984. Roscoe (1882), by the combustion of Cape diamonds, found 3·0007 $(O = 8)$, which Scott corrects to 2·9993. Richards and Hoover (1915) determined the ratio $Na_2CO_3 : 2Ag :: 29{\cdot}43501 : 59{\cdot}91676$. If the values $Ag = 107{\cdot}88$, $Na = 22{\cdot}966$ $(O = 16)$ are assumed, the equivalent of carbon is then found to be 3·001. On the basis $H = 1$, this gives 2·977.

The **volumetric composition** of carbon dioxide is found, approximately, in the same apparatus as was used in the case of sulphur dioxide (p. 491). A piece of pure charcoal is burnt in a confined volume of dry oxygen, over mercury. After cooling, it is found that the volume of the gas is practically unchanged. Thus, the number of molecules of carbon dioxide produced is equal to the number of molecules of oxygen disappearing, or one molecule of carbon dioxide contains one molecule of oxygen. The density of carbon dioxide, relative to hydrogen, is 21·97, hence its molecular weight is 43·94. This contains, however, a molecular weight of oxygen, viz., 31·76, so that the difference, 12·18, represents the carbon. Now it is found that a molecular weight of any volatile carbon compound never contains a smaller amount of carbon than 12 parts, so that 12·18 should be the atomic weight of carbon, and the formula of carbon dioxide is CO_2. The corresponding value determined by the gravimetric method is $2{\cdot}98 \times 4 = 11{\cdot}92$. The difference is appreciable. Berzelius (1811), who based his value for the atomic weight of carbon on the volumetric method just described, was therefore in error by as much as 2 per cent. This result, when pointed out by Dumas, shook the confidence of chemists in the atomic weights of Berzelius, but an active revision of these showed that, except in one or two cases, they were of a high order of accuracy.

The difference arises from the fact that carbon dioxide is more compressible than oxygen, so that there is a slight contraction when carbon is burnt in oxygen. Correct values would be found by the limiting density method (p. 147), but since the complete compressibility curve of carbon dioxide is not known at very low pressures, the method has been applied to carbon monoxide and to methane, which are more nearly perfect gases than the former. The result with both is **C = 11·910** (H = 1), in complete agreement with the result of the gravimetric method.

Percarbonates.—If a saturated solution of potassium carbonate is electrolysed at −10° to −15°, with a platinum anode enclosed in a porous cell, a bluish-white amorphous precipitate of **potassium percarbonate,** $K_2C_2O_6$, is deposited at the anode. This may be washed rapidly with cold water, alcohol, and ether, and dried over P_2O_5. The formation of the salt is represented as follows :



$$\begin{array}{l}\mathrm{KO\cdot CO\cdot OK}\\ \\ \mathrm{KO\cdot CO\cdot OK}\end{array} = 2\mathrm{K}^{\cdot} + \begin{array}{l}\mathrm{-O\cdot CO\cdot OK'}\\ \\ \mathrm{-O\cdot CO\cdot OK'}\end{array} = 2\mathrm{K} + \begin{array}{l}\mathrm{O\cdot CO\cdot OK}\\ \mid\\ \mathrm{O\cdot CO\cdot OK}\end{array}.$$

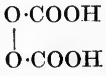
It is fairly stable at the ordinary temperature when dry, but is decomposed by water with evolution of oxygen. The sodium salt cannot be prepared by electrolysis, since sodium carbonate does not form a sufficiently concentrated solution. By the action of hydrogen peroxide on sodium carbonate a crystalline salt is obtained, which was formerly considered to have the composition $Na_2CO_4 + \frac{1}{2}H_2O_2 + H_2O$. It is now regarded as a carbonate containing **hydrogen peroxide of crystallisation :** $Na_2CO_3 + 1\frac{1}{2}H_2O_2$.

Potassium percarbonate, prepared by electrolysis, liberates iodine immediately from a cold solution of potassium iodide, a reaction considered to be characteristic of a **true percarbonate :** $K_2C_2O_6 + 2KI = 2K_2CO_3 + I_2$. The sodium compound and hydrogen peroxide behave alike in liberating iodine only *slowly*. By the action of carbon dioxide on a mixture of sodium peroxide and alcohol, **sodium percarbonate,** $Na_2C_2O_6$, is formed, which combines with sodium peroxide to form **sodium permonocarbonate,** Na_2CO_4. Both these salts, however, liberate less iodine than the equivalent of the active oxygen. A second potassium percarbonate, $K_2C_2O_6$, is prepared by the action of carbon dioxide on alcohol and potassium peroxide ; this resembles the sodium compound, and differs from potassium percarbonate obtained by electrolysis, in its action on potassium iodide.

Two **isomeric percarbonates,** therefore, appear to exist :

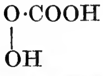
(α) KO·CO·O·O·CO·OK (*electrolytic*) ; (β) KO·O·CO·O·CO·OK (*from peroxide*).

The compound Na_2CO_4 is represented as NaO·O·CO·ONa. The salts $K_2C_2O_6$ and Na_2CO_4 are derived from **perdicarbonic, or percarbonic, acid,** analogous to perdisulphuric acid (p. 520), and **permonocarbonic acid,** corresponding with Caro's acid, respectively :



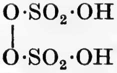
$$\begin{array}{l}\mathrm{O\cdot COOH}\\ \mid\\ \mathrm{O\cdot COOH}\end{array}$$

percarbonic acid



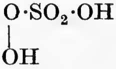
$$\begin{array}{l}\mathrm{O\cdot COOH}\\ \mid\\ \mathrm{OH}\end{array}$$

permonocarbonic acid



$$\begin{array}{l} O\cdot SO_2\cdot OH \\ | \\ O\cdot SO_2\cdot OH \end{array}$$

persulphuric acid



$$\begin{array}{l} O\cdot SO_2\cdot OH \\ | \\ OH \end{array}$$

permonosulphuric acid (Caro's acid)

By the action of phosphoric acid on potassium percarbonate in ether, an unstable solution of **percarbonic acid,** $H_2C_2O_6$, is formed. H_2CO_4 is not known.

The carbon dioxide cycle.—In very remote geological periods the atmosphere of the earth was probably very rich in carbon dioxide, whilst the primary rocks, such as felspar, $K_2O,Al_2O_3,6SiO_6$, consisted almost entirely of bases in combination with silica. At high temperatures, silica displaces carbon dioxide from carbonates, forming silicates. As the temperature fell, the carbon dioxide and water in the atmosphere began to decompose the silicates, with the formation of free silica (quartz), aluminium silicates (clay), soluble alkali carbonates, and bicarbonates of alkaline earths (*e.g.*, potassium carbonate, and calcium bicarbonate): $K_2O,Al_2O_3,6SiO_2 + CO_2 + 2H_2O = K_2CO_3 + Al_2O_3, 2SiO_2,2H_2O + 4SiO_2$. These soluble carbonates (*e.g.*, K_2CO_3) were partly retained in the soil formed by this **weathering,** or **pneumatolysis,** of the primary rocks, and were partly washed away to the sea.

Meanwhile, the water of the sea had come into equilibrium with the atmospheric carbon dioxide, and dissolved a portion of it. The calcium and magnesium bicarbonates were utilised by marine organisms, which retained the normal carbonates, and set free half the carbon dioxide, which was again evolved to the atmosphere. When the organisms died, the calcium carbonate of their shells was deposited in the form of **chalk beds,** or **coral reefs** (a process which is still going on), producing **sedimentary rocks.** In this way carbon dioxide was largely removed from the atmosphere, and stored up in the form of sedimentary rocks. It is estimated that, at present, about 30,000 times as much carbon dioxide is contained in rocks as exists free in the atmosphere.

The proportion of carbon dioxide in the atmosphere was thus considerably reduced, and further diminution occurred as a result of the growth of **green plants** under the influence of sunlight. The partial decomposition of the remains of these early plants led to the formation of **coal deposits,** in which the carbon is largely contained in the free state, or as hydrocarbons rich in carbon. The process of decomposition of carbon dioxide by green plants may now be considered.

Photosynthesis.—Green plants contain a pigment known as **chlorophyll,** which may be extracted by boiling alcohol. This pigment occurs associated with protoplasm in the form of corpuscles known as **chloroplasts,** which are the active agents in the decomposition of atmospheric carbon dioxide by plants under the influence of sunlight.

In the leaves of green plants are special organs through which atmospheric water vapour, oxygen, a little nitrogen, and carbon dioxide in aqueous solution pass into the cell sap. In aquatic plants the gases are absorbed entirely from solution. Oxygen and carbon dioxide are also exhaled by plants. Carbon dioxide is absorbed by all parts of the surface of the plant which contain chlorophyll, but mainly by the leaves, and it supplies the material from which the plant builds up its food. It is converted in the leaves, under the action of light, first into the carbohydrate **starch.** The net result of this change may be represented by the equation :

$$6x\text{CO}_2 + 5x\text{H}_2\text{O} + \text{energy of light} = (\text{C}_6\text{H}_{10}\text{O}_5)_x \text{ (starch)} + 6\text{O}_2.$$

The production of oxygen from carbon dioxide by the agency of living green plants under the influence of light was observed by Priestley, Ingenhouz, and Senebier, at the close of the eighteenth century ; it is readily demonstrated by experiment.

EXPT. 280.—Fill a flask with tap water and insert into the water some sprigs of watercress or mint. Fit the flask with a cork through which a funnel passes, fill the latter with water, and invert in it a test-tube full of water. Expose the flask to bright sunlight if available, otherwise to bright daylight. Bubbles of gas are produced on the leaves, which rise into the test-tube (Fig. 341). These are readily shown to consist largely of **oxygen.**

FIG. 341.—Production of Oxygen from Carbon Dioxide by Green Plants in Light.

The mechanism of the reactions by which this process is effected in the plant is unknown ; recent work has cast considerable doubt on all the theories previously entertained. The chlorophyll appears to absorb the light energy which is necessary for the reaction, and acts as a **photochemical sensitiser.** The reaction itself is called a **photosynthesis.**

The influence of light in promoting chemical changes was met with also in the union of hydrogen and chlorine (p. 234). In some cases the invisible **ultra-violet rays** of the spectrum are most active, and the violet end of the spectrum (p. 755) often appears to be more chemically active than the red, or intermediate, portions. Nevertheless, the name **actinic rays,** formerly given to the violet and ultra-violet parts of the spectrum, is inappropriate, since *all* the rays of the spectrum may be chemically active in different reactions.

The decomposition of carbon dioxide by the chlorophyll granules of plants is a case in point. It occurs most rapidly in red and yellow light, which are absorbed by the green chlorophyll. This part of the solar spectrum corresponds with the position of maximum energy for high sun, or the wave-length $666\mu\mu$.

Sulphuretted hydrogen is most rapidly decomposed by *red* light, and in some cases even the infra-red rays (so-called "heat rays") are most active. Light may also *retard* a chemical reaction: *e.g.*, the oxidation of alkaline pyrogallol (p. 719) is retarded by violet light, but accelerated by red light.

The oxygen absorbed by the plant furnishes the energy by which its ordinary life-processes are carried on, the light energy being concerned only with the photosynthesis. As a result of the vital processes, carbon dioxide is exhaled. Growth ceases in absence of oxygen: it is most rapid at temperatures of 22° to 37°, and ceases below 0°, or above 50°.

At night, in the absence of light, the photosynthesis is arrested, and the starch granules in the leaves pass out of the cells through the sieve vessels into the sap in the form of soluble carbohydrates such as **sugar,** $C_{12}H_{22}O_{11}$. The waste water is given off from the surface of the plant by transpiration.

The growth of plants.—The **food of plants** is entirely inorganic. Besides the **gases** mentioned above, plants require also **mineral matters,** which are absorbed in solution from the soil by the roots. These include combined nitrogen as nitrates, potassium, calcium, magnesium, and sodium salts, phosphates, chlorides, silica, and sulphur as sulphates. The normal soil always contains sufficient amounts of all these, except potassium salts, nitrates, and phosphates, which may have to be added in the form of **manures,** or **fertilisers.** Potassium salts are added in the form of nitre (occasionally), potassium chloride or sulphate, or the crude potash minerals of Stassfurt. Combined nitrogen is supplied in the form of Chile nitre, ammonium sulphate, blood, guano, and other nitrogenous animal products, and farmyard manure. It is in all cases converted before assimilation into nitrates by the activity of micro-organisms in the soil (*cf.* p. 563). Phosphates are supplied as soluble superphosphate of lime, basic slag, bones, or other phosphates which can be dissolved by the carbonic acid evolved by decaying vegetable matter (**humus**) in the soil.

Small quantities of iron, lithium, manganese, etc., also required, are taken from the soil. Absorption occurs by selective permeation of the dissolved salts through the membranes of the root-hairs. If plants are supplied with carbon dioxide, air, and light, and the roots are immersed in a solution containing the necessary elements (C, H, O, $N(NO_3')$, $S(SO_4'')$, $P(PO_4''')$, $Si(SiO_2$ aq.), Cl, K, Ca, Mg, Fe) they continue to grow. No organic matter is required.

The weights in lb. of the various mineral substances removed per acre by different crops are given below (R. Warington, "Chemistry of the Farm"):

	Ash.	N.	K_2O.	CaO.	MgO.	P_2O_5.	Cl.	SiO_2.	Na_2O.	S.
Wheat, 30 bushels	31	33	9·7	1·0	3·7	14·3	0·2	0·5	0·9	2·7
Straw, 28 cwt.	158	12	18·2	9·2	4·0	8·4	1·7	110·6	2·5	5·1
Barley, 40 bushels	46	35	9·8	1·3	4·0	16·2	0·4	12·0	1·0	2·9
Straw, 22cwt.	100	12	21·6	8·5	2·5	4·4	3·2	51·5	4·2	3·2
Oats, 45 bushels	54	38	8·5	2·0	3·9	11·8	—	24·8	1·4	3·2
Straw, 26 cwt.	140	14	29·6	9·8	5·3	7·1	5·5	69·3	5·9	4·8
Meadow hay, 1½ tons	208	49	56·3	28·1	10·1	12·7	16·2	57·5	11·9	5·7
Red clover hay, 2 tons	255	102	87·4	86·1	30·9	25·1	9·4	6·8	4·1	9·4
Turnips and leaves, 17 tons	364	120	148·8	74·0	9·5	33·1	22·1	7·7	24·5	20·9
Mangels and leaves, 22 tons	690	147	262·5	53·3	46·9	49·1	90·4	25·0	140·6	14·0

By the activity of green plants, and marine organisms, therefore, the carbon dioxide content of the atmosphere tends to be reduced. We must now consider those processes which tend to increase the atmospheric carbon dioxide. These are combustion and respiration.

Respiration.—Early experimenters, such as Mayow, Scheele, Priestley, and Lavoisier, were all aware of the great similarity between combustion and **respiration.** Lavoisier pointed out that the oxygen breathed into the lungs oxidises the carbonaceous materials of the blood, producing carbon dioxide, which is exhaled, and that **animal heat** is the result of this chemical process of oxidation.

The oxygen passes into the **lungs**; these consist of hollow sacs, the surfaces of which are separated from the blood-vessels by thin walls, through which the interchange of dissolved oxygen and carbon dioxide occurs. A certain amount of respiration takes place through the **skin**: this process is small in man, but is marked in animals such as frogs. In the case of fish, dissolved oxygen is absorbed by the **gills.**

The blood contains red corpuscles, composed of protoplasm with a colouring matter known as **hæmoglobin**; the latter contains iron in the form of organic compounds, but its exact composition is yet unknown. Hæmoglobin absorbs oxygen, producing a bright red substance, which exists in the blood of the arteries, passing from the lungs to the tissues. In the latter, the loosely-combined oxygen is absorbed, and oxidation processes occur. These are the source of animal heat and energy, and one of the products is carbon dioxide, which remains in solution as carbonic acid or bicarbonates. The de-oxygenated blood corpuscles have now a dark purple colour, and part of the blood containing them passes back to the heart by the veins, to be pumped to the lungs for re-aeration.

The volume of air passing into the human **lungs** at each inspiration, or the **tidal air,** amounts to about 500 c.c. ; in forced respiration it may reach 1640 c.c. The **stagnant air,** which remains in the lungs, and mixes with the tidal air, is about 1640 c.c. The **expired air** contains by volume 5 per cent. more carbon dioxide and 5 per cent. less oxygen than the inspired air. It amounts to 400 cu. ft , or 11,200 litres, per twenty-four hours, and conveys away from the organism about 9 ounces of water, and 8 ounces of carbon as carbon dioxide. Normal respiration in man occurs eighteen times per minute.

The expansion and contraction of the lungs, by which respiration occurs, are brought about by movements of the ribs, the muscles of which are controlled by a nervous centre situated in the *medulla oblongata,* or lower portion of the brain. This nervous centre is stimulated by the carbonic acid dissolved in the arterial blood passing through it, and the activity of the carbon dioxide appears to be due solely to its **acidity,** or the concentration of hydrogen ions in the blood. To maintain this acidity constant within very narrow limits is the function especially of the kidneys ; the carbonic acid is expelled in the lungs in the form of carbon dioxide.

In consequence of the activities of plants and animals, the first absorbing carbon dioxide from the atmosphere, retaining the carbon and excreting the oxygen, and the latter absorbing oxygen and excreting carbon dioxide, a kind of **balance** is maintained between the proportions of oxygen and carbon dioxide in atmospheric air.

Atmospheric carbon dioxide.—Normal outdoor air contains about 3 volumes of carbon dioxide per 10,000. The average figures for air at Kew are 2·43 (minimum)–3·60 (maximum). On Mont Blanc the figures are 2·62 at an altitude of 1080 m., and 2·69 at an altitude of 3050 m. In crowded towns, and especially in rooms not sufficiently ventilated, the proportion of carbon dioxide may rise to 0·3 per cent. by volume. The continued breathing of air containing 0·2 per cent. of CO_2 is injurious (Angus Smith). The "stuffiness" of badly ventilated spaces is chiefly the effect of the water vapour exhaled by the lungs, which tends to saturate the stagnant air, and impedes the evaporation of perspiration.

The total amount of carbon dioxide in the atmosphere corresponds with about 600,000 million tons of carbon. The **sources of atmospheric carbon dioxide** are : respiration of animals and plants, combustion, fermentation, putrefaction, the soil (worms, decay, and gas of volcanic origin), mineral springs, volcanic activity, and lime-burning. **Atmospheric carbon dioxide is diminished** by : absorption by the sea, photosynthesis by green plants, and the weathering of siliceous rocks ($1{\cdot}62 \times 10^9$ tons of CO_2 per annum). On the whole, the proportion of carbon dioxide in the atmosphere appears to be slowly increasing, and slight changes of climate may be due partly to this cause.

In the **estimation** of atmospheric carbon dioxide, a measured volume of air may be drawn by an aspirator, first through a drying tube containing pumice soaked in sulphuric acid, and then through a weighed tube containing soda-lime. This is followed by a tube of pumice and sulphuric acid to absorb moisture given off in the soda-lime tube, and the last two tubes are weighed together. A more convenient process is **Pettenkofer's method.** A measured volume of standard baryta water is shaken with a known volume of the air in a large (8–10 lit.) bottle, and the excess of baryta titrated with standard acid and phenolphthalein: $Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$. Absorption is more rapid with a hot solution of baryta.

EXAMPLE.—Volume of air taken in bottle = 2360 c.c. at 15° and 762 mm. 20 c.c. of baryta water required 18 c.c. $N/20HCl$ (1 c.c. = 0·558 c.c. CO_2) before, and 15·8 c.c. after, shaking with the air. Thus, volume of CO_2 at S.T.P. in the sample of air = $(18{\cdot}0 - 15{\cdot}8) \times 0{\cdot}558 = 1{\cdot}228$ c.c. Volume of sample at S.T.P.

$$= 2360 \times \frac{762}{760} \times \frac{273}{288} = 2237 \text{ c.c.};$$

hence percentage of CO_2 by volume $= \frac{1{\cdot}228 \times 100}{2237} = \mathbf{0{\cdot}055}.$

CARBON MONOXIDE, CO.

Carbon monoxide, CO.—Lassone (1776) obtained an inflammable gas by heating charcoal with zinc oxide; Priestley (1796) substituted iron-scales (Fe_3O_4) for zinc oxide. The latter experimenter considered the gas to be phlogisticated water, the water supposed to exist in the calx having combined with the phlogiston of the charcoal. These experiments were quoted as evidence against Lavoisier's antiphlogistic theory, according to which carbonic acid should have been formed. Cruickshank in 1800 found, however, that the gas was not inflammable air (hydrogen), but an oxide of carbon containing less oxygen than carbonic acid, and Clement and Desormes showed that it could be formed by passing the latter over heated charcoal. Dalton (1808) found that the gas requires half its volume of oxygen for combustion, and then forms carbonic acid: its formula is therefore CO.

Carbon monoxide occurs in coal gas and in some volcanic gases. It is formed during the combustion of charcoal or coke in a limited supply of air; the blue flames seen on the top of a clear fire consist of burning carbon monoxide. The presence of carbon monoxide in furnace gases is evidence of improper air supply, and its estimation in flue gases therefore affords a useful check on the furnace efficiency. Poisoning by the fumes of burning charcoal, described by Hoffmann in 1716, is due to carbon monoxide, which is a dangerous poison.

The production of carbon monoxide in a fire was formerly supposed to be due to the reduction of the carbon dioxide, formed from the lower portions of the glowing fuel and the entering air, by passing through the incandescent mass of carbon: $C + O_2 = CO_2$; $CO_2 + C = 2CO$. The monoxide burns on the top of the fire, where an excess of air is present. The researches of Dixon and H. B. Baker, however, point to carbon monoxide as a primary product in the combustion of carbon: $2C + O_2 = 2CO$. If carbon, carefully dried, is heated in oxygen dried by prolonged exposure to phosphorus pentoxide, principally carbon monoxide is formed according to Baker. Wheeler, however, states that both carbon monoxide and carbon dioxide are formed simultaneously under these conditions.

The reduction of carbon dioxide by carbon proceeds somewhat slowly, so that equilibrium: $C + CO_2 \rightleftharpoons 2CO$, is not usually attained in the combustion of carbon, and the composition of the resulting gas is variable. The following table contains the *equilibrium* values at atmospheric pressure for various temperatures.

$$CO_2 + C \rightleftharpoons 2CO$$

Temperature.	Per cent. CO_2 by vol.	Per cent. CO by vol.
850°	6·23	93·77
900°	2·22	97·78
950°	1·32	98·68
1000°	0·59	99·41
1050°	0·37	99·63
1100°	0·15	99·85
1200°	0·06	99·94

The formation of a *flame* of burning carbon monoxide when a diamond burns in a blast of air was noticed by Macquer in 1771; large quantities of carbon monoxide are also formed when a blast of air is forced through a thin bed of incandescent coke. The reduction of carbon dioxide by carbon occurs with appreciable velocity only at temperatures higher than 600°. The amount of monoxide formed in equilibrium increases with the temperature. The reverse reaction: $2CO = CO_2 + C$, was demonstrated by Deville (1864), who observed the deposition of carbon on a narrow, silvered copper tube placed axially in a strongly-heated porcelain tube through which carbon dioxide was passed. The copper tube was cooled by a stream of water.

EXPT. 281.—Pass a slow current of carbon dioxide over pieces of charcoal heated to redness in an iron tube (Fig. 342). The carbon dioxide is removed from the issuing gas by a tube of soda-lime, and the monoxide may then be burnt at a jet.

Carbon monoxide is formed by heating charcoal with zinc, iron, or manganese oxides: $C + ZnO = Zn + CO$, or with chalk or barium carbonate: $BaCO_3 + C = BaO + 2CO$. It is also produced by passing carbon dioxide over zinc dust or iron filings heated to redness in a glass tube: $CO_2 + Zn = ZnO + CO$. Calcium, magnesium, and the alkali-metals, on the other hand, lead to separation of free carbon: $2Ca + CO_2 = 2CaO + C$, and $4K + 3CO_2 = 2K_2CO_3 + C$.

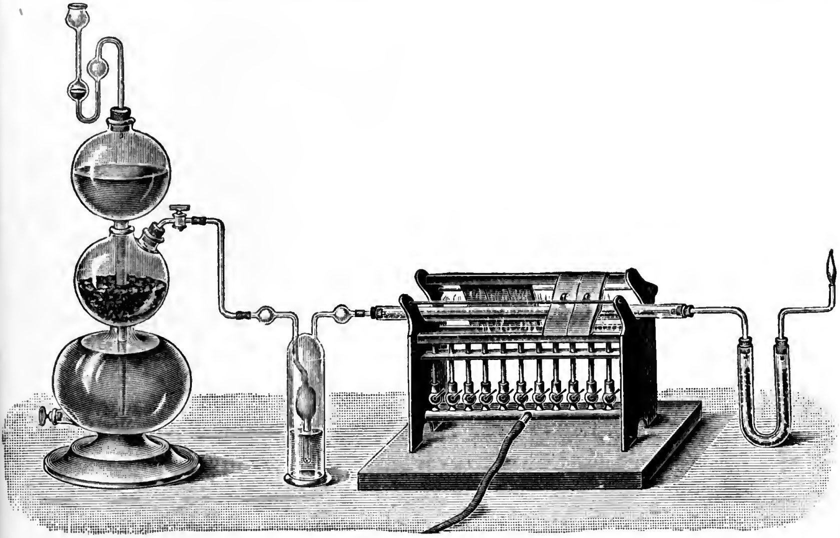


FIG. 342.—Carbon Monoxide from Carbon Dioxide and Carbon.

Preparation of carbon monoxide.—Although carbon monoxide is produced on the large scale by passing carbon dioxide over heated carbon (see p. 1002), in the laboratory it is more conveniently prepared by heating formic acid (or sodium formate), oxalic acid, or potassium ferrocyanide, respectively, with concentrated sulphuric acid.

The gas obtained from **formic acid** is almost perfectly pure: $H{\cdot}COOH = H_2O + CO$; a trace of sulphur dioxide may be formed in this, and in the following reactions, by reduction of the sulphuric acid: $H_2SO_4 + CO = CO_2 + SO_2 + H_2O$, but this is removed by washing with caustic soda.

Expt. 282.—Concentrated sulphuric acid is heated to 100° in a flask, and concentrated formic acid dropped in from a tap-funnel (Fig. 333). Cold concentrated sulphuric acid may also be dropped on dry sodium formate in a flask. The gas is washed with caustic soda, dried with phosphorus pentoxide, and collected over mercury. It is then pure.

Oxalic acid, when gently heated with concentrated sulphuric acid, evolves a mixture of equal volumes of carbon monoxide and dioxide: $(COOH)_2 = CO + CO_2 + H_2O$. The carbon dioxide is easily removed by washing with caustic soda.

Expt. 283.—Twenty-five gm. of crystallised oxalic acid ($C_2H_2O_4,2H_2O$) are covered in a flask with concentrated sulphuric acid. On heating gently, a brisk evolution of gas occurs. Fill a long tube divided into two parts by a paper label, and fitted with a stopcock, with the gas. Then attach a wash-bottle containing caustic soda solution to the generating apparatus, and collect jars of carbon monoxide over water. *Note: carbon monoxide is very poisonous.*

Admit a little caustic soda solution to the long tube of mixed gas, shake, and then open the stopcock under water. The latter rushes in and fills half the tube. Hence the gas contained half its volume of carbon dioxide.

Potassium ferrocyanide, on heating with ten times its weight of concentrated sulphuric acid in a large flask, evolves nearly pure carbon monoxide, but the reaction is usually somewhat violent:

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

The gas evolved in the later stages of the reaction is not pure.

Carbon monoxide is produced by withdrawing the elements of water from formic acid; this is effected by concentrated sulphuric acid, or by the catalytic action of metallic rhodium. The reverse reaction, *i.e.*, the synthesis of formic acid, is effected by the action of the silent discharge: $CO + H_2O \rightleftharpoons H{\cdot}CO{\cdot}OH$, and sodium formate is produced by passing carbon monoxide over caustic soda, or soda-lime, at 200°: $NaOH + CO = Na{\cdot}CO{\cdot}OH$. Carbon monoxide is, therefore, the **anhydride of formic acid.** The anhydride of oxalic acid, C_2O_3, does not exist, but breaks up at once into $CO + CO_2$.

Properties of carbon monoxide.—Carbon monoxide is a colourless gas with a peculiar faint smell. It is *very poisonous,* 10 c.c. per kg.

weight of an animal produces death, and the inhalation of air containing 1 vol. of CO in 800 vols. is fatal in half an hour. Coal gas (especially modern gas, which contains water-gas) owes its poisonous properties to the carbon monoxide it contains. The fumes of burning charcoal are lethal for the same reason.

The poisonous action of carbon monoxide depends on the absorption of the gas by the hæmoglobin of the blood, forming bright-red **carboxy-hæmoglobin**, which is a very stable substance. Oxygen is unable to displace carbon monoxide from the compound, and the animal dies because of lack of oxygenation of the blood and tissues. The absorption spectra (p. 762) of oxy-hæmoglobin and carboxy-hæmoglobin are similar but distinct, so that poisoning with carbon monoxide may readily be detected by examining the absorption spectrum of the blood. In cases of poisoning, artificial respiration and administration of oxygen should be resorted to at once, the patient being kept warm and at rest; alcohol may be given if there is a tendency to fainting.

Carbon monoxide is liquefied with difficulty; its critical temperature is − 140°. The liquid boils at −193°, and solidifies at − 200°.

The gas is sparingly soluble in water, but is readily absorbed by a solution of cuprous chloride in hydrochloric acid, a white crystalline compound, $CuCl,CO,2H_2O$, being formed. Water or ammonia must be present; a solution of cuprous chloride in dry alcohol does not absorb the gas.

The **composition** of carbon monoxide is determined by passing it over heated copper oxide, the carbon dioxide formed being absorbed in weighed potash-bulbs. The **normal density** of the gas is 1·2504, hence the relative density is 13·9, and the molecular weight 27·8 (approximately). The gas when mixed with half its volume of oxygen and exploded yields its own volume of carbon dioxide. The **formula** is therefore CO.

Many metals form compounds called **carbonyls**, with carbon monoxide: $Co(CO)_3$, $Co_2(CO)_8$, $Ni(CO)_4$, $Fe(CO)_4$, $Fe(CO)_5$, $Fe_2(CO)_9$, $Mo(CO)_6$, $Ru(CO)_x$. Carbon monoxide penetrates heated iron and may escape through the iron flues of stoves burning with an insufficient supply of air. Carbon monoxide also combines directly with chlorine, forming **carbonyl chloride** (*phosgene*), $COCl_2$.

Combustion of carbon monoxide.—Carbon monoxide burns in air or oxygen with a beautiful blue flame, forming carbon dioxide. The gas is also a powerful **reducing agent**, and when passed over heated metallic oxides it abstracts the oxygen contained in them, leaving the metal: $PbO + CO = Pb + CO_2$. Carbon monoxide is the active agent in a number of metallurgical processes (*cf.* the blast furnace). It reduces iodine pentoxide at 90°, with liberation of iodine: $I_2O_5 + 5CO = I_2 + 5CO_2$. This reaction may be used for the estimation of carbon monoxide in gases. A mixture of carbon monoxide and hydrogen may be analysed in this way, or by passing the mixture with oxygen over palladium-asbestos; only the hydrogen is oxidised. If a mixture of carbon monoxide and methane is passed over copper oxide at 250°, only the carbon monoxide is oxidised. If gas containing only 0·05 per cent. of CO is shaken with a solution of palladious chloride, a black precipitate of palladium is produced.

The explosion of carbon monoxide with oxygen.—A mixture of two volumes of carbon monoxide and one volume of oxygen explodes when lighted in the ordinary way. H. B. Dixon in 1880 found, however, that if the gases are carefully dried by exposure to phosphorus pentoxide, they cannot be exploded in a eudiometer, although combination occurs locally in the path of the electric sparks. If a trace of moisture, or of any gas which contains hydrogen, and so produces water on combustion in oxygen (CH_4, H_2S, etc.), is added, the mixture can be exploded by a spark. M. Traube (1885) found that a burning jet of carbon monoxide, dried by passing through towers containing glass beads wetted with very concentrated sulphuric acid, is extinguished when plunged into a jar of oxygen containing very strong sulphuric acid which has been dried by standing for a few hours carefully stoppered.

Girvan (1903) finds that 1 molecule of water in 24,000 of the gas is still active. The maximum effect is produced by 4·5 per cent. of water vapour.

The **catalytic influence of moisture** in this (and other similar) reactions is still somewhat obscure. Since carbon monoxide readily reduces steam at high temperatures: $CO + H_2O \rightleftarrows CO_2 + H_2$, Dixon supposes that this reaction first occurs, and that the hydrogen then combines with the oxygen present to reproduce water: $2H_2 + O_2 = 2H_2O$, and so on.

Catalytic effect of moisture.—Numerous cases of the catalytic effect of moisture are known. Dry chlorine does not combine with dry metals, except mercury. Dry carbon monoxide and oxygen do not explode on sparking. In the absence of moisture, to the extent produced by prolonged drying over phosphorus pentoxide, carbon combines only slowly with oxygen on heating; ammonium chloride and calomel volatilise on heating without dissociation; ammonia and hydrogen chloride do not combine on mixing; and sulphur and phosphorus may be distilled unchanged in oxygen. Nitrogen trioxide, after prolonged drying in the liquid state over P_2O_5, volatilises as N_4O_6; in presence of a minute trace of moisture this instantly dissociates into NO and NO_2. The boiling point of liquid N_4O_6 is also raised from $-2°$ to $+43°$ by drying for three years. Calomel dried for six months over P_2O_5 at

115° will not vaporise at all at 352°, when its usual vapour pressure is 347 mm.

In some cases the presence of *pure* water is not sufficient to catalyse a reaction, but a trace of impurity is needed.

H. B. Baker (1902) found that a mixture of very pure hydrogen and oxygen from the electrolysis of baryta, if sealed up in glass tubes over purified P_2O_5, *did* combine slowly, after prolonged drying, when the tube was heated with a flame, or if a spiral of silver wire was heated almost to the melting point in the gas, *but no explosion occurred.* The water produced by the combination was, according to Armstrong's theory (1885), too pure to form an electrically-conducting circuit, which he considers necessary for chemical change.

Producer gas.—The gaseous mixture obtained by passing air through a bed of incandescent coke, consisting principally of nitrogen and carbon monoxide, is made for heating purposes, and is called **producer gas** (or **air-gas**). The **producer** consists of a closed fire-grate in which coke rests on bars; it is often sealed below by water, and the *primary air* is either drawn through the fuel with a fan, or forced through by pressure, the ash-pit then being air-tight (Fig. 343). If the gas is burnt without cooling, the total amount of heat evolved is the same as if the carbon were burnt directly to carbon dioxide: usually 30 per cent. of the heat is lost by the producer gas cooling before it arrives at the place where it is burnt. Gas-firing is preferred for many purposes on account of the ease with which it is regulated and its cleanliness. The air admitted for the combustion of the producer gas is called *secondary air.*

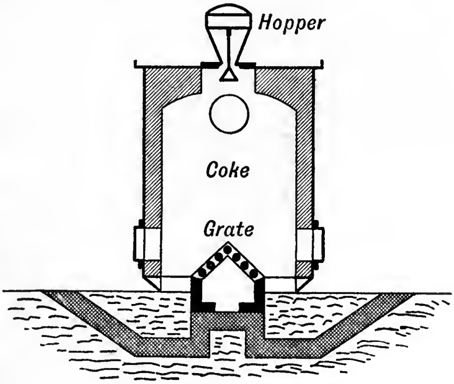


FIG. 343.—Gas Producer.

If coal is used instead of coke, the gas will be mixed with coal gas, unless the draught through the producer is downwards, when the coal gas is decomposed by the incandescent fuel. Otherwise the tar must be separated from the gas ("suction-gas"); with down-draught it is absent.

Water gas.—If steam is blown through incandescent coke, a mixture of carbon monoxide, carbon dioxide, and hydrogen is formed, known as **water gas**: (1) $C + H_2O \rightleftharpoons CO + H_2$; (2) $CO + 2H_2O \rightleftharpoons CO_2 + 2H_2$. The proportion of carbon monoxide increases as the temperature rises, as is seen from the following table, giving the results of Bunte:

Temp.	Percentage of steam decomposed.	Composition of gas by volume.			$\frac{CO}{CO_2}$	$\frac{H_2}{CO}$	$\frac{CO}{CO+CO_2}$
		H_2	CO	CO_2			
675°	8·8	65·2	4·9	29·8	0·16	13·3	0·141
758	25·3	65·2	7·8	27·0	0·29	8·4	0·224
840	41·0	61·9	15·1	22·9	0·65	4·1	0·397
955	70·2	53·3	39·3	6·8	5·80	1·35	0·853
1010	94·0	48·8	49·7	1·5	33·10	0·98	0·972
1060	98·0	50·7	48·0	1·3	36·8	1·04	0·975
1125	99·4	50·9	48·5	0·6	80·8	1·05	0·988

Average water gas has the following composition: H_2, 49·17; CO, 43·75; CO_2, 2·71; methane, 0·31; N_2, 4·00. Its **calorific power** is about 350 B.Th.U. per cu. ft., but as it requires only 2·5 vols. of air for combustion, it gives a very hot flame.

The reactions in the water gas producer absorb heat, hence the hot coke is gradually cooled by the steam blast, and the amount of carbon dioxide in the gas increases. When the *steam blast* has passed for a certain time (eight to twelve minutes), it is shut off, and an *air blast* turned on until the fuel is again heated to bright redness (one and a half to two minutes). The producer gas formed in the air-blow is utilised in raising steam, although extra fuel must be used for this purpose. To keep the temperature as uniform as possible, the steam blast is passed alternately upwards and downwards through the producer. In recent types, the fuel bed is thin, and carbon dioxide is largely formed during the air-blow.

Semi-water gas is prepared by passing a mixture of steam and air *continuously* through incandescent coke, the heat evolved by the combustion of the carbon with the oxygen of the air being sufficient to maintain the temperature for the water gas reaction to occur with the steam. About four times as much carbon is burnt by the air as reacts with the steam. **Mond gas** is formed with a large excess of steam which keeps the temperature low (650°), and allows of the recovery as ammonia of a larger proportion of the nitrogen of the coal-slack used than if the coal had been heated in retorts.

Carburetted ("enriched") **water gas** is formed by mixing water gas with hydrocarbons, partly unsaturated, which burn with a luminous flame. Water gas alone (*i.e.*, a mixture of hydrogen, carbon monoxide, and nitrogen) burns with a blue, non-luminous flame, but may be used with Welsbach mantles for illuminating purposes, since it gives out a considerable amount of heat on combustion. In the manufacture of carburetted water gas, two towers packed with chequer-brickwork are placed after the producer. The first, called the **carburetter,** and the second, called the **superheater,** are first heated to redness by the hot producer gas from the air-blow passing down the first and up the second. The water gas from the steam-blow is now passed through the towers. Into the carburetter a spray of mineral oil is injected. This vaporises, and the mixture of water gas and oil vapours then passes through the red-hot bricks in the superheater, where the oil vapour is decomposed, or "cracked," with the formation of permanent gases rich in ethylene. The gas is then scrubbed and collected. **Pintsch gas** is formed by spraying oil into hot retorts and passing the gas through a condenser, scrubber, and lime purifier.

The compositions of two typical specimens of semi-water gas (producer gas) are given below, together with an analysis of true water gas :

	CO.	H_2.	CH_4.	CO_2.	O_2.	N_2.
Dowson gas from coal ..	25·07	18·73	0·62	6·57	—	49·01
Do. from coke..	22·40	7·00	—	4·90	0·50	65·20
Mond gas from coal ..	13·20	24·80	2·30	12·90	—	46·80
Water gas	39·6	51·9	0·8	4·2	—	2·9

The calorific power of producer and semi-water gas is very low, being usually about 125 B.Th.U. per cu. ft., as compared with about 600 for good coal gas. The adulteration of modern coal gas by water gas has considerably reduced its calorific value.

The following **thermal constants** are useful in fuel calculations :

(1) 1 lb. of carbon burning to carbon dioxide evolves 14,544 B.Th.U.

(2) 1 lb. of carbon burning to carbon monoxide evolves 4351 B.Th.U.

(3) 1 lb. of carbon reacts with steam to produce water gas ($C + H_2O = CO + H_2$) with the *absorption* of 4298 B.Th.U.

(4) 1 lb. of hydrogen burns to liquid water with the evolution of 60,626 B.Th.U.

(5) 1 lb. of carbon monoxide burning to dioxide evolves 4368 B.Th.U.

Hydrogen from water gas.—The **manufacture of hydrogen** from water gas is carried out in different ways : the carbon dioxide is first removed by washing with lime, and the carbon monoxide then separated by one of the following processes :—

(1) Washing with cuprous chloride solution, or with hot concentrated caustic soda under pressure : $CO + NaOH = H{\cdot}COONa$ (**sodium formate**) ;

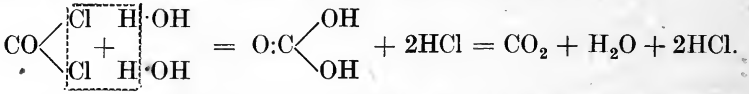
(2) passing over calcium carbide at 300° ; CO gives CaO and $CaCO_3$; nitrogen forms calcium cyanamide, $CaCN_2$ (p. 544) ;

(3) liquefaction of carbon monoxide by compression and cooling; the residual gas contains 2 per cent. of CO, removable by process (2);

(4) passing over lime, alone or mixed with oxide of iron, heated to 400–500°: $CaO + CO + H_2O = CaCO_3 + H_2$;

(5) mixing with steam and passing over finely-divided nickel or cobalt at 350–400°, or under 4–40 atm. at 300–600° in presence of nickel, iron, cobalt, or other catalyst. A little oxygen is added to maintain the temperature of the catalyst: $CO + H_2O \rightleftarrows CO_2 + H_2$. If CO_2 is added, the formation of CO from deposited carbon: $C + H_2O \rightleftarrows CO + H_2$, is prevented by mass-action.

Carbonyl chloride, or phosgene, $COCl_2$.—When a mixture of equal volumes of carbon monoxide and chlorine is exposed to bright sunlight, or passed over heated animal charcoal, direct combination occurs, with the formation of **carbonyl chloride,** or **phosgene,** $COCl_2$ (Greek, *phos,* light, and *gennac,* I produce). This compound, discovered by John Davy in 1811, is a colourless gas with a penetrating and suffocating odour, and is very poisonous. It is readily liquefied by cooling, forming a colourless, mobile liquid, b.-pt. 8°. The gas does not fume in moist air, but is readily hydrolysed by water. The hypothetical carbonic acid, H_2CO_3, may first be produced:



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{Cl} & \mathrm{H}\cdot\mathrm{OH}\\ & + \\ \mathrm{Cl} & \mathrm{H}\cdot\mathrm{OH}\end{matrix}\right. = \mathrm{O{:}C}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. + 2HCl = CO_2 + H_2O + 2HCl.$$

Phosgene is, therefore, the **chloride of carbonic acid.** When the gas is passed into a solution of ammonia in toluene, **urea** is formed, which may be regarded as the diamide of carbonic acid, or **dicarbamide,** $CO(NH_2)_2$: $COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl$. Both urea and ammonium chloride are precipitated, but may be separated by warming with alcohol, in which urea is soluble. The alcoholic solution deposits, on evaporation and cooling, crystals of urea.

The monamide of carbonic acid, $\mathrm{CO}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}\right.$, is called **carbamic acid.** Its ammonium salt, $\mathrm{CO}\left\langle\begin{matrix}\mathrm{O\cdot NH_4}\\ \mathrm{NH_2}\end{matrix}\right.$, is contained, together with ammonium bicarbonate, NH_4HCO_3, in commercial "carbonate of ammonia" (p. 801).

Carbonyl bromide, $COBr_2$, is slowly formed from carbon monoxide and bromine vapour.

Carbonyl sulphide, or carbon oxysulphide, COS.—This compound, discovered by Than in 1867, is formed when carbon monoxide and sulphur vapour are passed through a heated tube : $CO + S \rightleftharpoons COS$, or when sulphur dioxide is passed over red-hot charcoal. It is most conveniently prepared by the action of diluted sulphuric acid (5 vols. of H_2SO_4 to 4 vols. of water) on ammonium thiocyanate, NH_4CNS, at 20°. The unstable thiocyanic acid appears first to be formed, and is hydrolysed by water : $HCNS + H_2O = COS + NH_3$. The gas so prepared contains hydrocyanic acid, HCN, and carbon disulphide. The first is removed by passing through very concentrated caustic potash solution ; the latter by passing through concentrated sulphuric acid followed by a mixture of triethyl phosphine, $P(CH_3)_3$, pyridine, and benzene.

Carbonyl sulphide is a colourless, odourless gas, sparingly soluble in water, but readily soluble in toluene. It liquefies at 0° under 12 atm. pressure, b.-pt. $-50{\cdot}2°$; m.-pt. $-138{\cdot}2°$. It is very inflammable, a glowing chip causing its ignition, and burns with a blue, slightly luminous, flame. When mixed with oxygen, it explodes feebly with a spark, even after drying with phosphorus pentoxide, although neither carbon monoxide nor sulphur burns when perfectly dry : $2COS + 3O_2 = 2CO_2 + 2SO_2$. A heated platinum spiral decomposes the gas without change of volume into sulphur and carbon monoxide : $COS = CO + S$ (solid).

The aqueous solution of carbonyl sulphide is slowly hydrolysed : $COS + H_2O \rightleftharpoons HO{\cdot}CO{\cdot}SH \rightleftharpoons CO_2 + H_2S$. The intermediate substance, $HO{\cdot}CO{\cdot}SH$, is **thiolcarbonic acid** (p. 715). The hepatic waters of Harkány and Parád, in Hungary, appear to contain carbon oxysulphide. Carbonyl sulphide is absorbed by dilute aqueous or alcoholic potash with the formation of a mixture of sulphide and carbonate : $COS + 4KOH = K_2CO_3 + K_2S + 2H_2O$.

Formic acid, H·CO·OH.—The absorption of carbon monoxide by heated alkalies, with the production of formates, has already been mentioned. At 120°, under 3 to 4 atm. pressure, the gas is rapidly and completely absorbed by a concentrated solution of caustic soda : $NaOH + CO = H{\cdot}COONa$. Large amounts of **sodium formate** are prepared by this method. From this, anhydrous **formic acid**, $H{\cdot}CO{\cdot}OH$, is obtained cheaply and in quantity. Thirty-five parts of concentrated sulphuric acid are run into 200 parts of concentrated formic acid, with shaking. To this mixture 50 parts of sodium formate and 50 parts of concentrated sulphuric acid are added alternately and the liquid distilled.

Formic acid is a colourless liquid, sp. gr. 1·226, b.-pt. 100·6°, m.-pt. 8·43°, with a pungent odour. It acts violently on the skin, raising blisters. The acid is contained in red ants (*Formica rubra*), and was first obtained from them by distillation in steam. It is also present in nettles, and in nearly all stinging organisms.

Formates are powerful reducing agents. If mercuric oxide is dissolved in dilute formic acid, it goes into solution as mercuric formate. This is soon reduced to a white precipitate of mercurous formate, and finally to grey metallic mercury. The formic acid is oxidised to carbon dioxide. In presence of ruthenium, rhodium, and iridium, especially if traces of the sulphides are present, formic acid decomposes into carbon dioxide and hydrogen: $H_2CO_2 = CO_2 + H_2$. The reverse reaction occurs on electrolytic reduction with a clean zinc cathode, or by passing hydrogen through a solution of a bicarbonate containing palladium or platinum.

If a mixture of sodium formate with one-twentieth of its weight of caustic soda is heated to 250–260°, hydrogen is evolved, and **sodium oxalate** remains: $2HCO_2Na = (CO_2Na)_2 + H_2$. From sodium oxalate free **oxalic acid,** $(CO_2H)_2,2H_2O$, is easily obtained. By the electrolytic reduction of oxalic acid, **glyoxylic acid,** $H{\cdot}CO{\cdot}CO_2H$, and finally **glycollic acid,** $H_2(OH)C{\cdot}CO_2H$, are obtained in large quantities. All these organic compounds, therefore, may be obtained directly from carbon monoxide.

Carbon suboxide, C_3O_2.—If malonic acid, $CH_2(COOH)_2$, or ethyl malonate, $CH_2(COO{\cdot}C_2H_5)_2$, is treated with a large excess of phosphorus pentoxide at 300° under 17 mm. pressure, **carbon suboxide,** C_3O_2, is evolved. The reaction with malonic acid is: $CH_2(COOH)_2 = C_3O_2 + 2H_2O$; that with ethyl malonate is: $CH_2(COO{\cdot}C_2H_5)_2 = C_3O_2 + 2H_2O + 2C_2H_4$.

The gas evolved is liquefied by cooling, and is fractionated; the carbon suboxide boils at 6°. It freezes in liquid air to a white solid, m.-pt. $-$ 111·3°. The gas has a pungent odour, and is poisonous. It burns in air with a smoky flame, and explodes with oxygen when ignited: $C_3O_2 + 2O_2 = 3CO_2$. The liquid slowly polymerises at the ordinary temperature, forming a red solid insoluble in water, and the gas decomposes rapidly on heating or in contact with phosphorus pentoxide. Carbon suboxide dissolves readily in water, forming a solution of **malonic acid,** of which it is the second anhydride, *i.e.*, formed by the removal of *two* molecules of water from one molecule of the acid. Its formula is, therefore, O:C:C:C:O. The gas is readily soluble in benzene and xylene.

Carbon disulphide, CS_2.—Sulphur vapour when passed over red-hot carbon produces **carbon disulphide,** CS_2, a volatile liquid, the reaction being endothermic and reversible: $C + 2S \rightleftharpoons CS_2 - 25{\cdot}4$ kgm. cal. Since heat is absorbed in the reaction, the yield is improved by working at a high temperature, and the compound is now largely manufactured in the electric furnace. Carbon disulphide was discovered by Lampadius in 1796, by heating pyrites with charcoal.

In the older process a vertical cast-iron or fireclay retort is set in a furnace and filled with charcoal (Fig. 344). Sulphur is fed in through a side tube, *a*, at the base of the retort, being kept fused by the waste heat. The sulphur volatilises, and the vapour passes over the white-hot charcoal, forming carbon disulphide. The vapours pass through a small iron cylinder, *d*, where sulphur is deposited, and the carbon disulphide is condensed in a very long worm-tube cooled by water.

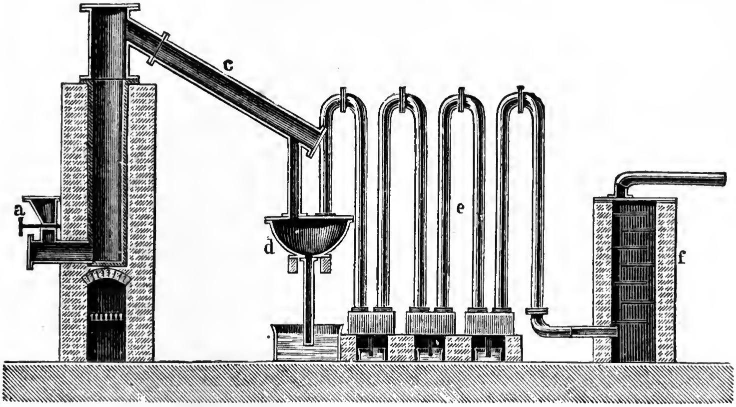


FIG. 344.—Manufacture of Carbon Disulphide.

In Taylor's electrical process (1899) a tower 40 ft. high and 16 ft. in diameter (Fig. 345) is packed with charcoal or coke from the top. Below this is a furnace with four carbon electrodes, between alternate pairs of which an arc is struck. The sulphur in the lower part of the furnace melts and evaporates, the vapour passing through the heated coke above the arc, and forming carbon disulphide. Fresh coke and sulphur are added every twelve hours through the hoppers shown. The disulphide is condensed as before, and purified by redistillation. It is further purified by agitation with mercury, and redistilled over white wax.

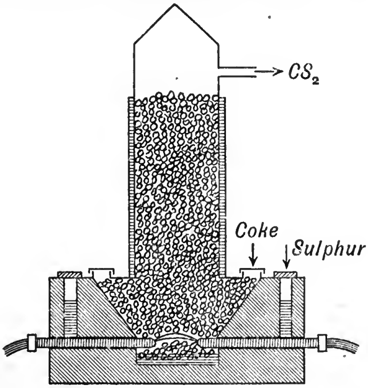


FIG. 345.—Taylor's Electric Carbon Disulphide Furnace.

EXPT. 284.—A combustion tube packed with small pieces of recently ignited charcoal is fitted in a sloping combustion furnace as shown in

Fig. 346. The lower end is connected with bulb tubes surrounded by ice. When the tube is red hot, bits of sulphur are introduced into the upper end, which is corked. The sulphur vapour passes over the hot charcoal, and the carbon disulphide formed (containing sulphur in solution) is collected in the bulbs.

Properties of carbon disulphide.—Carbon disulphide is a colourless, mobile, strongly refracting liquid, which boils at 46°, solidifies at − 116°, and remelts at − 110°. Its density at 0° is 1·2923. The liquid is slightly soluble in water, the solubility diminishing with rise of temperature. One hundred c.c. of water dissolve 0·204 gm. of CS_2 at 0°, 0·179 at 20°, and 0·014 at 40°. Carbon disulphide readily volatilises, and its vapour has an exceedingly unpleasant odour, which is not removed by careful purification (Dixon). The vapour ignites at a very low temperature: a test-tube filled with hot oil held over the liquid in a dish sets fire to the vapour. The vapour forms a violently explosive mixture with oxygen, the most violent explosion being obtained with $2CS_2 + 5O_2 = 2CO + 4SO_2$. Sulphur dioxide, sulphur trioxide, carbon monoxide, and carbon dioxide are formed. No free carbon is deposited.

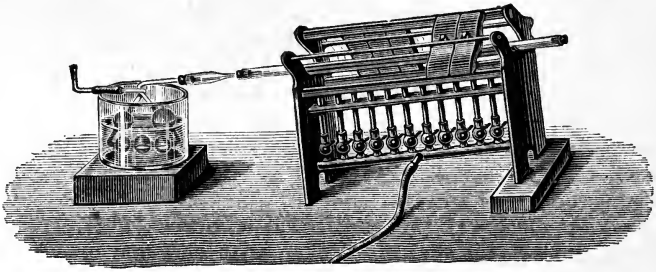


FIG. 346.—Preparation of Carbon Disulphide.

Carbon disulphide, being an endothermic compound, is unstable at the ordinary temperature. If a little mercury fulminate is exploded in a tube filled with the vapour, decomposition commences, with separation of sulphur and carbon, but is not propagated through the vapour.

Carbon disulphide mixes with absolute alcohol, ether, and oils. It also dissolves sulphur, white phosphorus, indiarubber, camphor, resins, etc., and is largely used as a solvent.

The vapour is decomposed by heated potassium: $CS_2 + 4K = 2K_2S + C$. When chlorine is passed into boiling carbon disulphide containing a little iodine, **carbon tetrachloride,** CCl_4, is formed:

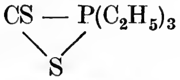
$$CS_2 + 3Cl_2 = CCl_4 \text{ (b.-pt. 77°)} + S_2Cl_2 \text{ (b.-pt. 136°)}.$$

Both products of this reaction are useful, and are separated by fractional distillation. Carbon tetrachloride is used, under the name of *pyrex*, as a grease solvent, and for extinguishing fires.

Carbon disulphide vapour acts as a powerful poison when inhaled: it is used to kill moths in furs, etc., and mice and rats in grain elevators.

A mixture of carbon disulphide vapour and hydrogen, when passed over heated platinised pumice, or nickel at 450°, yields hydrogen sulphide: $CS_2 + 2H_2 = C + 2H_2S$ (p. 682).

This reaction is used in determining the amount of CS_2 in coal gas: the H_2S produced is estimated by passing the gas through a solution of lead nitrate in sugar syrup, and matching the brown tint of the PbS with standards.

Carbon disulphide reacts with an ethereal solution of triethyl phosphine, $P(C_2H_5)_3$, forming a red crystalline compound $P(C_2H_5)_3,CS_2$, possibly with the constitution  .

When the vapour of carbon disulphide is passed over red-hot copper, carbon is deposited and copper sulphide formed: $CS_2 + 4Cu = C + 2Cu_2S$. It was in this way that the composition of the substance was first determined by Vauquelin. A mixture of the vapour with steam, or sulphuretted hydrogen, when passed over red-hot copper, gives **methane**:

$$CS_2 + 2H_2O + 6Cu = CH_4 + 2Cu_2S + 2CuO;$$
$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S.$$

From methane, organic substances such as alcohol and acetic acid may be obtained, so that these reactions allow of the **synthesis** of such compounds, carbon disulphide being prepared directly from its element. (Berthelot, 1856.)

Carbon subsulphide, C_3S_2.—This compound, corresponding with the suboxide C_3O_2, was discovered by Lengyel. It is formed by striking an arc under carbon disulphide, the cathode being of carbon and the anode of antimony containing 7 per cent. of carbon. The liquid is then distilled *in vacuo*, and the vapour condensed at − 40°. A yellowish-red solid is formed, m.-pt. − 0·5°. It has the composition C_3S_2, and the structural formula is probably S:C:C:C:S, similar to that of C_3O_2. The vapour has an offensive odour, and produces a copious flow of tears. A **dibromide**, $C_3S_2Br_2$, is formed directly, and has a not unpleasant aromatic smell.

Carbon monosulphide, $(CS)_x$, is said to be contained in the brown powder produced when carbon disulphide is exposed to light. **Thiocarbonyl chloride,** $CSCl_2$, is formed when a mixture of carbon disulphide, chlorine, and a trace of iodine is heated in a sealed tube for some time, or when a mixture of phosphorus pentachloride and carbon disulphide is heated in a sealed tube at 100°: $PCl_5 + CS_2 = PSCl_3 + CSCl_2$. It is a liquid, boiling at 149° with slight decomposition, has a very offensive odour, and is slowly hydrolysed by water. When treated with nickel carbonyl, solid $(CS)_x$ is formed.

Carbon sulphoselenide, CSSe, and **sulphotelluride,** CSTe, have been prepared by striking an arc under carbon disulphide between a graphite cathode and an anode of graphite and selenium, or tellurium, respectively. They are yellow and red liquids, respectively.

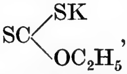
Thiocarbonic acid.—If carbon disulphide is agitated with a concentrated solution of caustic soda it slowly dissolves. The solution contains sodium carbonate, and a new salt, **sodium thiocarbonate,** Na_2CS_3, which may be regarded as the carbonate in which oxygen is replaced by the analogous element sulphur :

$$3CS_2 + 6NaOH = 2Na_2CS_3 + Na_2CO_3 + 3H_2O.$$

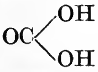
If a solution of sodium sulphide is used instead of caustic soda, the reaction is more rapid, and sodium thiocarbonate alone is formed : $Na_2S + CS_2 = Na_2CS_3$. On adding alcohol, the thiocarbonate separates as a heavy oily liquid of slightly brown colour. On treating this with cold dilute hydrochloric acid, free **thiocarbonic acid,** H_2CS_3, separates as a yellow oil, decomposed on warming into sulphuretted hydrogen and carbon disulphide : $H_2CS_3 = H_2S + CS_2$. A deep red solution and yellow crystals of the ammonium salt, $(NH_4)_2CS_3$, are formed when carbon disulphide and concentrated ammonia are allowed to stand together for a few days. The relationship between these and the corresponding compounds containing oxygen is obvious, and was pointed out by their discoverer, Berzelius (1825) :

Anhydride . .	CO_2		CS_2	
Acid . .	H_2CO_3	$(H_2O + CO_2)$	H_2CS_3	$(H_2S + CS_2)$
Salt . .	K_2CO_3	$(K_2O + CO_2)$	K_2CS_3	$(K_2S + CS_2)$

Thiocarbonates are used in destroying *phylloxera*, a fungus infesting vines. Carbon disulphide is a poison for this fungus, but it is too volatile to use directly ; if the plants are sprayed with a solution of sodium thiocarbonate, this is slowly decomposed by atmospheric carbonic acid, with liberation of carbon disulphide.

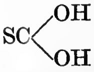
If carbon disulphide is dissolved in alcoholic potash, a salt of the composition  $SC\begin{cases} SK \\ OC_2H_5 \end{cases}$, known as **potassium xanthate,** is formed. It is decomposed by acids, with liberation of carbon disulphide and alcohol, $C_2H_5{\cdot}OH$; this reaction indicates that the ethyl radical in the compound is attached to oxygen, and not to sulphur.

From carbonic acid, by successive replacement of oxygen by sulphur, a series of acids results :



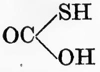
$\mathrm{OC}{<}^{\mathrm{OH}}_{\mathrm{OH}}$

carbonic acid



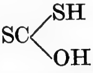
$\mathrm{SC}{<}^{\mathrm{OH}}_{\mathrm{OH}}$

thion-carbonic acid



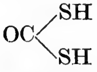
$\mathrm{OC}{<}^{\mathrm{SH}}_{\mathrm{OH}}$

thiol-carbonic acid



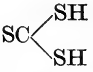
$\mathrm{SC}{<}^{\mathrm{SH}}_{\mathrm{OH}}$

thiol-thion-carbonic acid



$\mathrm{OC}{<}^{\mathrm{SH}}_{\mathrm{SH}}$

dithiol-carbonic acid



$\mathrm{SC}{<}^{\mathrm{SH}}_{\mathrm{SH}}$

thiocarbonic acid

Thiocarbonates give a brown precipitate, $CuCS_3$ with copper salts ; a red precipitate $PbCS_3$, with lead salts ; and a yellow precipitate, Ag_2CS_3, with dilute silver nitrate. These rapidly become black, from formation of sulphides. Ferric salts give an intense red colour. By the action of hydrochloric acid on ammonium thiocarbonate, carbon oxysulphide is evolved.

Carbon disulphide dissolves very readily in solutions of alkali disulphides, forming **perthiocarbonates** : $Na_2S_2 + CS_2 = Na_2CS_4$.

Cyanogen, C_2N_2.—By heating cyanide of silver, Gay-Lussac (1815) obtained a gas which burns with a peach-blossom coloured flame. This is **cyanogen,** C_2N_2: $2AgCN = 2Ag + C_2N_2$.

Cyanogen is produced by heating the cyanides of silver, mercury, and gold, the most convenient being mercuric cyanide, $Hg(CN)_2$, which is heated to dull redness in a hard glass or steel tube : $Hg(CN)_2 = Hg + C_2N_2$. A heavy, brown, non-volatile powder is produced at the same time, called **paracyanogen ;** it is probably a polymerised form of cyanogen, $(CN)_n$, and decomposes slowly into cyanogen at 310°. The gas is evolved at a lower temperature if mercuric chloride is mixed with the cyanide : $Hg(CN)_2 + HgCl_2 = 2HgCl + C_2N_2$.

EXPT. 285.—Heat a little mercuric cyanide in a hard glass tube fitted with a rubber stopper and glass jet. Ignite the gas at the jet ; it burns with a characteristic peach-blossom coloured flame. *N.B.—Cyanogen is very poisonous.*

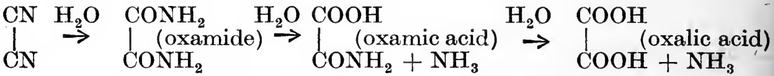
The most economical method for the preparation of cyanogen is to drop a concentrated solution of potassium cyanide into a warm solution of 2 parts of crystallised copper sulphate dissolved in 4 parts of water. **Cupric cyanide,** $Cu(CN)_2$, is first formed as a yellow precipitate, but this quickly decomposes, with evolution of cyanogen gas, leaving white **cuprous cyanide,** CuCN : $2CuSO_4 + 4KCN = 2K_2SO_4 + 2CuCN + C_2N_2$. If the cuprous cyanide is collected and treated with ferric chloride solution, the rest of the cyanogen is evolved : $2CuCN + 2FeCl_3 = 2CuCl + 2FeCl_2 + C_2N_2$.

Cyanogen is apparently formed directly from its elements when an arc is struck between carbon poles in nitrogen : $2C + N_2 \rightleftharpoons C_2N_2$; it can be detected by the spectrum, but is decomposed in contact with carbon and cannot be separated from the arc-gases. Cyanides are also produced by the action of nitrogen on carbides at high temperatures. Thus, if nitrogen is passed over barium carbide, or an intimate mixture of barium oxide and carbon, at a red heat, **barium cyanide** is produced. The compound **barium cyanamide,** $BaCN_2$, is first formed: (1) $BaO + C = Ba + CO$. (2) $Ba + 2C = BaC_2$. (3) $BaC_2 + N_2 = BaCN_2 + C$. (4) $BaCN_2 + C = BaC_2N_2$. Cyanogen is present in blast-furnace gas in small quantities. It is an endothermic compound: $2C$ (graphite) $+ N_2 = C_2N_2 - 70$ kgm. cal.

Properties of cyanogen.—Cyanogen is a colourless gas which is very soluble in water, and must therefore be collected over mercury. It has a smell of bitter almonds, and is very poisonous. When cooled it condenses to a colourless liquid, boiling at − 20·7°, which freezes below − 35° to a white solid, melting at − 34·4°. The density of the gas shows that it has the formula C_2N_2.

Cyanogen is absorbed by a solution of caustic potash, with the formation of **potassium cyanide,** KCN, and **potassium cyanate,** $KCNO$: $C_2N_2 + 2KOH = KCN + KCNO + H_2O$. With water at 0° the reaction $C_2N_2 + H_2O = HCN + HCNO$ occurs. From the similarity of these reactions to those with chlorine (p. 368), and from the fact that all compounds of cyanogen contain the univalent cyanogen group, or radical, CN, the latter is sometimes written Cy, since it behaves to some degree as an element. In solutions of cyanides the **cyanide ion,** CN', is split off: $KCN \rightleftharpoons K^{\cdot} + CN'$.

A solution of cyanogen in water decomposes on standing, with deposition of a brown precipitate of **azulmic acid,** $C_4H_5N_5O$: the solution then contains ammonium oxalate, hydrocyanic acid, HCN, urea, carbon dioxide, etc.



$$\begin{array}{l}CN\\|\\CN\end{array} \xrightarrow{H_2O} \begin{array}{l}CONH_2\\| \text{ (oxamide)}\\CONH_2\end{array} \xrightarrow{H_2O} \begin{array}{l}COOH\\| \text{ (oxamic acid)}\\CONH_2 + NH_3\end{array} \xrightarrow{H_2O} \begin{array}{l}COOH\\| \text{ (oxalic acid)}\\COOH + NH_3\end{array}$$

A mixture of equal volumes of cyanogen and oxygen explodes on ignition or with an electric spark, even when carefully dried over phosphorus pentoxide, with the production of carbon monoxide and nitrogen: $C_2N_2 + O_2 = 2CO + N_2$; with double the volume of oxygen, carbon dioxide is formed: $C_2N_2 + 2O_2 = 2CO_2 + N_2$.

The formula of cyanogen may be written as $N\vdots C{\cdot}C\vdots N$, with nitrogen tervalent, or as $C\vdots N{\cdot}N\vdots C$, with nitrogen quinquevalent.

Hydrocyanic acid, HCN.—When potassium cyanide (p. 793) is distilled with a mixture of equal volumes of sulphuric acid and water, the vapour of **hydrocyanic acid,** HCN, is evolved:

$$KCN + H_2SO_4 = KHSO_4 + HCN.$$

With concentrated sulphuric acid, carbon monoxide is formed in large quantities, according to the equation: $HCN + 2H_2O = H{\cdot}COOH + NH_3 = H_2O + CO + NH_3$. The gas is dried by a U-tube of calcium chloride, and passed through a second U-tube cooled in ice. A colourless liquid, boiling at 26·1° and freezing at − 15°, collects. This is **anhydrous hydrocyanic acid.** The vapour burns with a purple flame in air. The anhydrous acid is also produced by passing sulphuretted hydrogen over dry mercuric sulphide heated to 30° in a long glass tube, and condensing the liquid in a freezing mixture. Hydrocyanic acid is formed when acetylene is sparked with nitrogen: $C_2H_2 + N_2 = 2HCN$, or when a mixture of nitrogen and hydrogen is passed through a carbon arc:

$$2C + H_2 + N_2 \rightleftharpoons 2HCN.$$

Anhydrous hydrocyanic acid is one of the most dangerously poisonous substances known, and its preparation should be undertaken only by expert chemists. A dilute solution may be prepared by distilling potassium ferrocyanide with *dilute* sulphuric acid (7 acid + 14 water); the $2\frac{1}{2}$ per cent. solution is used as a constituent of remedies for bronchial catarrh, etc., and is called **prussic acid.** In this concentration it is also very poisonous.

Hydrocyanic acid is a very weak monobasic acid: its salts with alkali metals, the **cyanides,** are hydrolysed in solution. They show an alkaline reaction, and smell of peach-kernels owing to the presence of the free acid: $KCN + H_2O \rightleftharpoons KOH + HCN$.

The smell of bruised fruit kernels, laurel leaves, and moist bitter almonds is due to hydrocyanic acid, and it is a curious fact that Scheele, the discoverer of hydrocyanic acid (1782), did not know of its poisonous properties: these were first suspected from its formation from the poisonous bitter almonds, by distillation with water. Ammonia, or chlorine water, is used as an antidote to the acid, although large doses are almost instantaneously fatal.

Hydrocyanic acid in solution appears to exist in two forms, or **tautomeric modifications**: $H{\cdot}C{\vdots}N \rightleftharpoons H{\cdot}N{\vdots}C$. Two series of compounds with organic radicals, the **cyanides,** $R{\cdot}C{\vdots}N$, and **isocyanides,** $R{\cdot}N{\vdots}C$, are known, corresponding with the two hypothetical acids.

Cyanogen chloride, CNCl.—If chlorine is passed into anhydrous hydrocyanic acid, **cyanogen chloride,** $CN{\cdot}Cl$, is formed, which may be condensed in a freezing mixture to a colourless mobile liquid, b.-pt. 15·5° (Berthollet, 1787). The liquid, if slightly acidified, rapidly polymerises to white, solid, **cyanuric chloride,** $(CNCl)_3$. Cyanogen chloride reacts with alkalies, forming a chloride and a **cyanate**: $CN{\cdot}Cl + 2KOH = KCl + KCNO + H_2O$. It is the chloride of **cyanic acid,** HCNO. With ammonia, it forms **cyanamide,** $CN{\cdot}NH_2$.

Bromine and iodine react with hydrocyanic acid or potassium cyanide to form white crystalline **cyanogen bromide,** $CN\cdot Br$, and **cyanogen iodide,** $CN\cdot I$, respectively. The latter often occurs as an impurity in crude iodine. All the halogen compounds of cyanogen are very poisonous.

Tests for cyanides.—(1) A solution of a cyanide gives with silver nitrate a white curdy precipitate of **silver cyanide,** $AgCN$, soluble in concentrated nitric acid. (2) To the solution of the cyanide caustic soda is added, and a few drops of a mixed solution of ferrous sulphate and ferric chloride: on warming a **ferrocyanide** is produced: (*a*) $FeSO_4 + 2KCN = K_2SO_4 + Fe(CN)_2$; (*b*) $4KCN + Fe(CN)_2 = K_4Fe(CN)_6$. The dirty-brown precipitate produced is warmed with concentrated hydrochloric acid, which dissolves the ferric hydroxide present, and leaves a dark blue residue of **Prussian blue** (p. 995), formed by the action of the ferrocyanide on the ferric salt. If only traces of cyanides are present, a blue or green coloration appears. This test will detect 1 part of HCN in 50,000 parts of water. (3) The solution is evaporated to dryness on a water-bath with yellow ammonium sulphide, when a **thiocyanate,** *e.g.*, KCNS, is formed: $(NH_4)_2S_2 + KCN = KCNS + (NH_4)_2S$ (volatile). The residue is dissolved in water and ferric chloride solution added: a blood-red coloration of **ferric thiocyanate,** $Fe(CNS)_3$, is formed. This test is very sensitive.

Cyanates.—Potassium, or sodium, cyanide, in a state of fusion, is a powerful **reducing agent**: metallic oxides are converted into the metals, and a **cyanate** is formed: $KCN + PbO = KCNO + Pb$. The cyanate may be extracted with water. When the solution is acidified, **cyanic acid,** HCNO, is formed, but is almost completely decomposed by the water present, with formation of ammonia, and evolution of carbon dioxide: $HCNO + H_2O = NH_3 + CO_2$.

Ammonium cyanate, NH_4CNO, obtained by mixing concentrated solutions of potassium cyanate and ammonium chloride, is readily converted on heating into the isomeric compound **urea**: $NH_4\cdot CNO = CO(NH_2)_2$. This reaction, discovered by Wöhler in 1828, definitely broke down the hypothetical barrier dividing "inorganic" substances from "organic" substances, the latter supposed to be produced only by the agency of the "vital force." The distinction between inorganic and organic chemistry is now merely one of convenience. Previously to Wöhler's discovery, urea had been obtained by John Davy from phosgene and ammonia (p. 708), but he was not aware of the nature of the products of the reaction.

FLAME.

Flame.—A **flame** is a zone in which chemical combination between gases is occurring, accompanied by the evolution of heat and light: briefly, it is composed of glowing gas (Van Helmont, 1648). Transparent gases, such as nitrogen or oxygen, do not glow when heated in tubes to a high temperature, nor do burning solids emit flame unless a vapour is formed. Thus, iron burns in oxygen without a flame; carbon burns in air at low temperatures without a flame, but at high temperatures, when carbon monoxide is formed, the latter burns with a flame. A flame of pure hydrogen, burning in dust-free air, does not emit a visible light.

Flame is only produced in chemical reactions when a considerable amount of energy is liberated, although **chemiluminescence,** which may be regarded as a cold flame, can be induced at fairly low temperatures in many cases. Thus, if ether is dropped on a hot iron plate, so that ignition does not result, a greenish phosphorescent flame is seen in a dark room.

EXPT. 286.—Thirty c.c. of 30 per cent. hydrogen peroxide are added to a mixture of 10 c.c. of 10 per cent. pyrogallol solution, 20 c c. of saturated potassium carbonate solution, and 10 c.c. of commercial formaldehyde in a dark room. An orange-red glow, accompanied by a vigorous reaction, is seen. Light of the wave-length emitted is found to accelerate the reaction, which involves the oxidation of the pyrogallol.

Unless the combustible gas and the supporter of combustion are mixed before kindling the flame, the latter is **hollow,** and occupies only the surface of contact of the two gases. This may be shown by many experiments.

EXPT. 287.—Depress a piece of new asbestos paper on a Bunsen flame: a hollow dark ring is formed by the section of the flame. This may be seen also if a piece of ordinary paper is *quickly* lowered on to the flame.

EXPT. 288.—Thrust a match-head quickly inside a Bunsen flame; or support the match, head upwards, in the metal tube by a pin stuck through it, and then kindle the flame. The match-head does not ignite for a considerable time.

EXPT. 289.—Stretch a piece of fine wire gauze over a funnel, and place a *small* heap of gunpowder in the centre of it (Fig. 347). Pass a rapid stream of hydrogen through the funnel, and ignite the gas from above. The powder remains in the centre of the flame without explosion. If an unlighted match is thrust quickly through the flame to the powder, there is still no ignition, but if the flame is slowly turned down, the match ignites, and the gunpowder explodes.

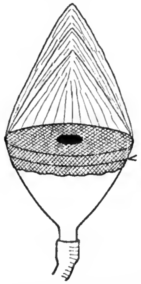


FIG. 347.—Experiment to Demonstrate that a Flame is Hollow.

EXPT. 290.—Insert one end of a glass tube into the middle portion of a Bunsen flame. Unburnt gas passes up the tube, and may be kindled at the upper end.

The terms **combustible** and **supporter of combustion** are purely relative, and depend simply on which gas is inside and which outside the flame. This has already been illustrated in the case of oxygen and hydrogen and hydrogen and chlorine.

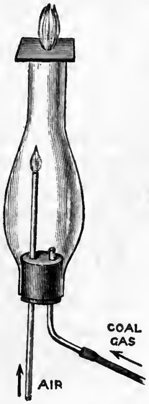


FIG. 348.—Air Burning in Coal Gas.

EXPT. 291.—A lamp chimney (Fig. 348) is fitted with a cork at the lower end, through which pass a wide straight tube and a narrow tube bent at a right angle. The top of the chimney is extended by a tin tube with a flat top pierced by a hole as shown. Coal gas is passed in through the bent tube, and may be kindled at the top of the glass, burning with a luminous flame. At the same time, air is drawn in through the wide tube, and if a lighted taper is passed up through this tube into the chimney, the air ignites and burns in the coal gas with a blue non-luminous flame. If the top flame is extinguished, and a taper passed down to the air-flame, it cannot be kindled, since it is surrounded by an atmosphere of coal gas, which will not support combustion of the hydrocarbons of the taper. A jet of air, however, may be ignited.

If the upper flame is again kindled, and the supply of coal gas gradually reduced, the upper flame shrinks and becomes less luminous, whilst the lower flame increases in size. The increase in size of the lower flame is due to the circumstance that the oxygen has now a more limited supply of coal gas available, and the combustion has therefore to extend over a larger area. Finally the upper flame goes out, partly on account of the larger proportion of carbon dioxide in the gas, and partly because a greater proportion of the coal gas is burnt by the lower flame.

EXPT. 292.—Arrange the lamp chimney with a large hole on the top, and two tubes below, as shown in Fig. 349. Pass the gas from a large Bunsen burner through the tube *A*, and kindle a large flame at the top of the glass. Push the tube *B* to the upper part of this flame, and pass a slow stream of oxygen through it. Lower *B* carefully, when it will be seen that a second flame of oxygen is burning inside the first flame, the oxygen combining with the unburnt gas in the centre of the large hollow flame.

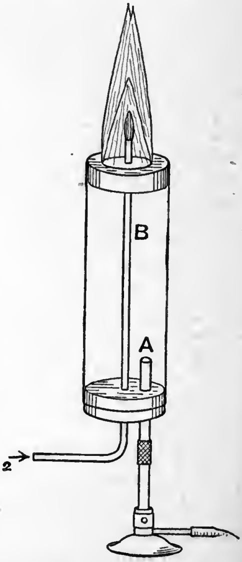


FIG. 349.—Oxygen Burning inside a Coal Gas Flame.

A very accurate account of the structure of flame was given by Hooke (" Lampas," 1677). He speaks of " that transient shining body which we call flame " as " nothing but the parts of the oyl rarified and raised by heat into the form of a vapour or smoak, the free air that encompasseth this vapour keepeth it into a cylindrical form, and by its dissolving property preyeth upon those parts of it that are outwards . . . producing the light which we observe ; but those parts which rise from the wick which are in the middle are not turned to shining flame till they rise towards the top of the cone, where the free air can reach and so dissolve them. With the help of a piece of glass [pressed upon the flame] anyone will plainly perceive that all the middle of the cone of flame neither shines nor burns, but only the outer superfices thereof that is contiguous to the free and unsatiated air."

This description refers to a candle or oil-lamp flame. The candle and lamp consist of a cotton **wick**, surrounded by the combustible material. The liquid oil, or the wax melted by heat, rises in this wick by capillary attraction. The top of the wick becomes incandescent, and the fuel is subjected to destructive distillation, the combustible gases burning with a flame. The action of the wick is peculiar.

EXPT. 293.—Attempt to kindle a piece of lump-sugar by a taper : the sugar melts but will not take fire. Now rub a corner of the sugar with a small quantity of cigarette ash : the sugar can then readily be lighted at that point and burns with a flame.

In the old tallow candle the wick acquired a deposit of soot, which required " snuffing " : the wick of the modern paraffin-wax candle is plaited so that it bends over, and is continuously consumed in the outer part of the flame. The action of the wick is probably two-fold : it presents the combustible material to the heated zone in a divided state, owing to its capillary structure, and it prevents too rapid conduction of heat away from the heated point where distillation occurs.

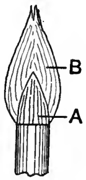


FIG. 350.—Structure of Hydrogen Flame (two cones).

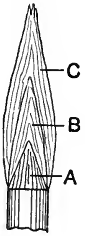


FIG. 351.—Structure of Carbon Disulphide or Ammonia Flame (three cones).

The structure of flame.—A **hydrogen flame** burning in air or oxygen consists (Fig. 350) of *two* cones, an inner one, *A*, of unburnt gas, and an outer one, *B*, in which the simple chemical reaction $2H_2 + O_2 = 2H_2O$ is occurring, with evolution of heat and light. The **flame of ammonia** burning in oxygen (p. 548) consists, however, of *three* cones, an inner cone, *A* (Fig. 351), of unburnt gas, surmounted by a yellow cone, *B*, in which decomposition of ammonia into its elements is taking place : $2NH_3 = N_2 + 3H_2$, and an outer pale greenish-yellow cone, *C*, in which the hydrogen burns. The nitrogen largely escapes combustion. A flame of **carbon disulphide** vapour in oxygen or air is similar to the ammonia flame : the cone *B* is lilac in colour, and corresponds with the reaction : $2CS_2 + O_2 = 2CO + 4S$, whilst the cone *C* is deep blue and represents complete combustion of carbon monoxide and sulphur.

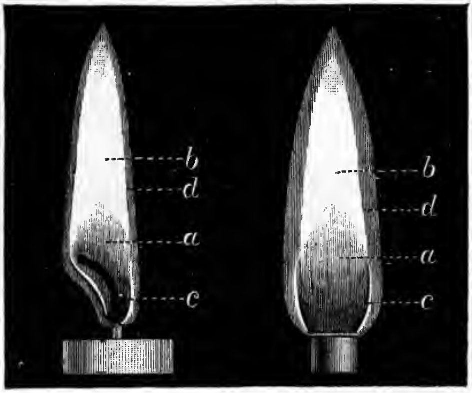


FIG. 352.—Structure of Hydrocarbon Flames.

Hydrocarbon flames are more complicated, and contain *four* regions, first defined by Berzelius. If the flame of a candle or of coal gas burning at a jet (Fig. 352) is examined, it is found to consist of (*a*) the dark inner cone of unburnt gas, or vapour of partly decomposed wax ; (*b*) a yellowish-white, brightly luminous region, occupying most of the flame ; (*c*) a small bright blue region at the base of the flame ; (*d*) a faintly-luminous outer mantle, surrounding the flame completely. If the supply of gas is reduced, the flame shrinks down, the luminous area *b* gradually disappearing, whilst the region *c* becomes continuous, and constitutes an inner cone (Fig. 353). The regions *a* and *d* remain.

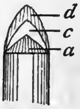


FIG. 353.—Small Hydrocarbon Flame with Continuous Blue Region *c*.

The luminosity of flame.—The question now arises : Why are the flames of a candle, coal gas, and ethylene, for instance, luminous, whilst those of hydrogen and carbon monoxide are non-luminous ? There are three theories to account for the luminosity of flame :

(1) **Davy's theory** (1816), which ascribed the luminosity to particles of **solid carbon** heated to incandescence in the flame. The origin of the carbon was explained later by Faraday on the incorrect assumption that the hydrogen of hydrocarbons burns preferentially to carbon, and the latter is deposited.

(2) **Frankland's theory** (1861), according to which the luminosity is due to incandescent **vapours of dense hydrocarbons** in the flame.

(3) **Lewes's theory** (1892), which considers the solid carbon in the flame to be the result of the thermal decomposition of ethylene and **acetylene** : $C_2H_4 = C_2H_2 + H_2 = 2C + 2H_2$.

Davy's investigations on flame.—Sir Humphry Davy in 1815 was led to the study of flame by an investigation of the causes and prevention of the disastrous fire-damp explosions in coal mines, which were prevalent when open candle flames were used by the miners. These are caused by the ignition of mixtures of methane and air (*fire-damp*) ; or, as we now know, sometimes by the kindling of a mixture of very fine coal-dust itself with air. Davy made the discovery that if a flame is cooled it is extinguished, and he recognised that combustible gases have different **ignition points.**

FIG. 354.—Principle of Safety Lamp.

EXPT. 294.—Lower a spiral of thick copper wire over a candle flame : the latter is extinguished. Now heat the spiral to redness, and repeat the experiment : the flame continues to burn.

EXPT. 295.—(i) Depress a piece of fine wire gauze over a Bunsen flame. The flame at first does not pass through the gauze, owing to the cooling effect caused by conduction of heat through the metal, and a red-hot ring is seen on the gauze, with a dark patch in the centre corresponding with the central unburnt portion of gas in the flame. That unburnt gas from the central part of the flame is passing through the gauze may be seen by holding a taper above the latter. If the experiment is repeated, and the gauze allowed to remain on the flame a sufficiently long time, the temperature of the metal rises to the ignition point, when the gas ignites and burns above the gauze.

(ii) If a piece of gauze, turned up at the edges, is held over an unlighted Bunsen burner, the gas passing through may be kindled above the gauze, but the flame does not pass through and light the gas at the burner. On raising the gauze, the flame flickers and finally goes out (Fig. 354). This flame, in which air is mixed with gas before combustion, is blue and non-luminous.

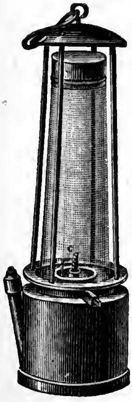


FIG. 355.—Davy's Safety lamp.

These experiments led Davy to the invention of the **safety-lamp,** which consists of an oil lamp having an enclosed cylinder of wire gauze as a chimney (Fig. 355). If this is taken into a mine where fire-damp exists, the latter will penetrate inside the gauze and burn there, but the flame is not propagated to the gas outside, because the heat is conducted away by the metallic gauze. The gauze may even become red hot from the mixture of gas and air burning inside, but as the ignition temperature of methane is high, the flame does not pass through to the gas outside. It has been found, however, that a draught of air blowing on the lamp may cause one portion of the gauze to become so hot as to result in ignition of the fire-damp, and the flame inside may also be blown mechanically through the gauze by a blast of air, passing at a rate exceeding 8 ft. per sec., such as is formed on firing a shot in a mine. With these exceptions the lamp, especially in its improved form, with a strong glass cylinder below the gauze, which permits of better illumination, is perfectly safe. The introduction of the safety-lamp, at first strongly opposed by some miners, has proved a great boon to workers exposed to fire-damp in the mine. If only a small amount of fire-damp is present in the air, a flame appears over the flame of the lamp, and, from the size of this **flame-cap,** the amount of combustible gas in the air may be ascertained.

EXPT. 296.—Lower a lighted Davy lamp into a large beaker into which some ether has been poured. The interior of the lamp is seen to be filled with flame, but the ether vapour in the beaker is not ignited.

Davy supposed that the **luminosity** of a hydrocarbon flame was due to " the decomposition of a part of the gas towards the interior of the flame, where the air was in smallest quantity, and the deposition of **solid charcoal,** which first by its ignition, and afterwards by its combustion, increases to a high degree the intensity of the light." The non-luminosity of the flame in the second part of Expt. 291 was due, according to Davy, to the carbon particles burning, as fast as produced, in the oxygen supplied.

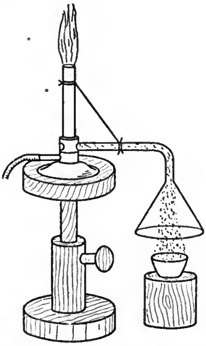


FIG. 356.—Bunsen Flame rendered Luminous by Smoke from Burning Camphor.

Flames known to contain solid particles, *e.g.*, those of zinc, magnesium, and potassium in oxygen, are very luminous, and the presence of solid particles of carbon in luminous hydrocarbon flames is definitely proved by the fact that a powerful beam of light is reflected by such a flame, and the reflected light is polarised (p. 8). The presence of carbon particles is also made probable by the following experiments :

EXPT. 297.—Hold a cold piece of pipeclay tube in a candle flame. Carbon is deposited on the lower part only, not on the top.

EXPT. 298.—Clouds of soot evolved from burning camphor, if admitted to the lower part of a Bunsen flame through one air-hole by means of a funnel tube (Fig. 356), render the flame luminous. Powdered charcoal sprinkled into a Bunsen flame also increases its luminosity.

Faraday accepted Davy's theory, but instead of supposing that the carbon arose from the decomposition of the gas by heat, he put forward the theory of the **preferential combustion of hydrogen** in the flame, with separation of unburnt carbon, which burnt subsequently, *e.g.*: $C_2H_4 + O_2 = 2H_2O + 2C$; $2C + 2O_2 = 2CO_2$. Hydrogen was supposed to have a greater affinity for oxygen than was exhibited by carbon. But Dalton had already shown that if ethylene is exploded with its own volume of oxygen, all the carbon is burnt to carbon monoxide, whilst the hydrogen is set free: $C_2H_4 + O_2 = 2CO + 2H_2$. Faraday's theory is therefore untenable.

EXPT. 299.—The structure of a candle flame is well shown by the following experiment, due to Faraday. A bent glass siphon is lowered into the candle flame (Fig. 357). With the tube just above the wick, dense white vapours pass over, and condense in the flask to solid wax: these correspond with the first process in the flame, the volatilisation of the solid wax by the heat, which occurs on the wick. This corresponds with the dark central portion of the flame. On raising the tube into the bright central portion of the flame, dense black vapours pass over, which deposit particles of carbon in the flask. On raising the tube still further, the black smoke disappears, and steam and carbon dioxide pass along the siphon. The former condenses to liquid water in the flask, and if a little lime-water is poured in, the presence of carbon dioxide is readily proved.

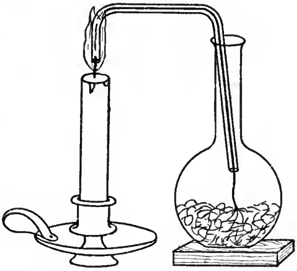


FIG. 357.—Faraday's Experiment to Illustrate the Structure of a Candle Flame.

Frankland's theory.—Sir Edward Frankland in 1861 noticed that the flame of a candle burning on the summit of Mont Blanc emitted a much feebler light than when it was burnt in the valley at Chamonix, although the rate of combustion was the same in both cases. In further experiments he found that a candle flame when burning under a partially evacuated receiver was much less luminous than in free air. This had been noticed by Boyle. An alcohol flame burning in compressed air is luminous. Again, a mixture of hydrogen and oxygen exploded in a eudiometer burns with a bright flash, and hydrogen burning in oxygen under 20 atm. pressure gives a luminous flame. The luminosity of the electric spark in gases increases with the density of the gas. Luminous flames are known in which solid particles cannot be present, *e.g.*, the flame of arsenic in oxygen, and of sodium in chlorine. As a result of his experiments, Frankland suggested that the luminosity of hydrocarbon flames was not due to the deposition of solid particles of carbon, as Davy had supposed, but to the presence of **dense gaseous hydrocarbons,** which became incandescent. The presence of solid carbon in flames has, however, definitely been proved, although Frankland's theory may apply to flames in which solid matter cannot be present.

Lewes's theory.—By aspirating and analysing the gases from different parts of the flame, V. B. Lewes in 1892 found that the unsaturated hydrocarbons (ethylene and acetylene) disappear only slowly in the dark portion, but rapidly in the luminous zone. The proportion of acetylene, however, increases rapidly as the gases pass up the dark zone, attaining 70 per cent. of the unsaturated hydrocarbons at the apex of the dark cone. Lewes assumes that ethylene is decomposed by heat, with the intermediate formation of acetylene : $C_2H_4 \rightarrow C_2H_2 + H_2 \rightarrow 2C + 2H_2$. The presence of free hydrogen has been detected in the luminous zone. The carbon is separated as a fine powder, and the heat of decomposition of the endothermic acetylene assists in raising the temperature.

The reaction in the bright blue part of the flame appears to be the same as that in the inner cone of a Bunsen flame (see below); in the outer, faintly visible, cone complete combustion of hydrogen and carbon monoxide occurs, as in the outer cone of the Bunsen flame.

The present position of the theory of luminosity of flames may be summed up in the statement that probably all three causes described by the theories of Davy, Frankland, and Lewes contribute to the luminosity.

The Bunsen flame.—If coal gas is mixed with a sufficient supply of air *before* combustion, as in the familiar Bunsen burner, it burns with a non-luminous flame. This now consists only of *two cones*: (1) a pale blue inner cone, which becomes green when a large supply of air is admitted, and the flame " roars " (as in the Téclu burner); (2) a still paler blue outer cone. The reactions in the inner cone are different from the purely thermal decompositions taking place in an ordinary flame, since partial oxidation now occurs, with formation of carbon monoxide. This burns in the outer cone.

Expt. 300.—The effect of admixture of air on the flame of a combustible gas may be studied with the apparatus shown in Fig. 358, due to Smithells. Undiluted carbon monoxide passed in through one of the lower tubes burns above with a hollow cone of blue flame (*a*), which is typical of what Smithells calls a **volume flame**. If a little air is admitted the cone becomes shorter, and its inner lining bright blue (*b*). With continued addition of air, a mixture is finally produced through which a flame would be propagated without external air, but the flame is kept on the top of the tube by the speed of the gas current (*c*). More air causes the speed of propagation of flame through the mixture to exceed the speed of the gas current, and at this point the **inner cone separates from the outer cone** in the flame, and passes down the tube (*d*). At a certain point the outer cone vanishes, and all the gas now burns in the inner cone (*e*). Now the rate of propagation of flame has been diminished by the excess of air added, and the lower flame is a double cone, as in the first case. When the rate of inflammation has been reduced below the rate of flow of gas, the flame again rises to the top of the tube (*f*), and burns as a single cone with a considerable unburnt inner space, typical of a **surface,** or **film, flame**.

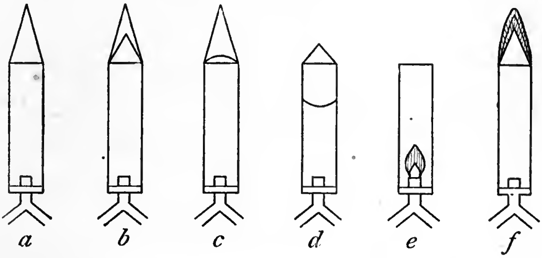


FIG. 358.—Smithells's Experiments on Flames.

EXPT. 301.—The separation of the two cones of a Bunsen flame is most conveniently effected by means of **Smithells's flame-cone separator** (1892). This consists (Fig. 359) of one glass tube sliding inside a wider tube. A mixture of air and gas (*e.g.*, methane), in regulated proportions, is passed into the central tube through stopcocks at the bottom. The central position of the inner tube may be kept by a brass guide fitted to it or by passing it somewhat loosely through a cork in the wider tube, as shown. If the quantity of air supplied is increased, the Bunsen flame burning at the top separates into two cones, one of which remains on the outer tube, and the other, which is the inner cone of the complete flame, passes down and burns on the top of the narrower tube. By raising the latter, the inner cone may be joined to the outer one, and the complete flame raised outside on the inner tube.

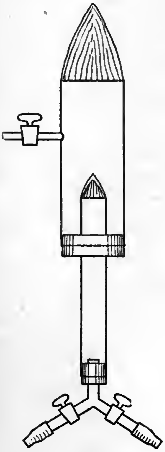


FIG. 359.—Smithells's Flame-cone Separator.

By analysing the **interconal gas,** drawn off from the space between the two cones by a side tube shown, it was found to consist of nitrogen from the air, carbon monoxide, carbon dioxide, steam, and hydrogen. The composition of the mixture was the same if pure methane, containing no hydrogen, were used, and it is evident that the reaction taking place in the inner cone of the Bunsen flame leads to the incomplete burning of the hydrocarbon, with formation of carbon monoxide and hydrogen (p. 674), and with the excess of oxygen, when some carbon dioxide is formed, an **equilibrium,** $CO + H_2O \rightleftharpoons CO_2 + H_2$, is set up between the carbon monoxide, steam, carbon dioxide, and hydrogen. This is known as the **water-gas equilibrium.** The law of mass-action leads to the following relation between the concentrations :

$$\frac{[CO] \times [H_2O]}{[CO_2] \times [H_2]} = K.$$

This relation was shown to hold for the water-gas equilibrium by Dixon in 1884 ; Smithells, and later Haber, find that the same relation holds for the interconal gases of a flame, and the constant K has the value corresponding with the temperature of the latter.

The **temperatures of flames** have been determined in various ways (*e.g.*, by platinum and platinum-rhodium thermocouples), and the following values have been found (Féry, 1904) :

Bunsen, fully aerated	1871°	Oxy-coal-gas blowpipe	2200°
,, insufficient air	1712°	Oxy-acetylene blowpipe	2420°
Acetylene	2548°	Oxy-acetylene explosion	3000–4000°
Alcohol	1705°	[Electric arc	3760°]
Hydrogen, free flame...	1900°	[Sun	7800°]

The cause of the **non-luminosity of the Bunsen flame** has been attributed to three circumstances :—

(1) **Oxidation :** Davy's theory, already considered. That this is at least only a partial explanation follows, however, from the experiments described below.

(2) **Dilution :** Blochmann found that not only oxygen, but also inert gases, such as nitrogen, carbon dioxide, or even steam, will render the flame of coal gas non-luminous in the Bunsen burner.

Expt. 302.—Stop up one air-hole at the base of the burner, and connect the other with an apparatus for generating carbon dioxide. Light the coal gas, and then gradually admit carbon dioxide : the flame becomes non-luminous, but consists of only *one* cone instead of two, as in the ordinary Bunsen flame.

Lewes states that 1 volume of coal gas requires the following proportions by volume of inert gases to render it non-luminous : CO_2, 1·26 ; N_2, 2·30 ; CO, 5·11 ; H_2, 12·4. The flame was rendered non-luminous by 0·5 vol. of oxygen, or 2·27 vols. of air. That the effect cannot be due to cooling entirely is evident from the effect of carbon monoxide, which gives a much hotter flame than coal gas.

(3) **Cooling:** Wibel showed, however, that cooling the flame resulted in loss of luminosity.

Expt. 303.—Bring a cold flat-iron in contact with the flame of coal gas burning in a fishtail burner. The flame loses its luminosity.

Expt. 304.—Suspend a platinum crucible in a Bunsen flame which has been rendered just luminous by adjusting the air-holes, whilst the crucible is red hot. Now pour cold water in the crucible; the flame will be seen to lose its luminosity.

Expt. 305.—Attach a tube formed by rolling platinum foil round a glass tube to the top of a Bunsen burner, and light the flame at the top of the platinum tube. Heat the latter to redness by another Bunsen flame; the first flame becomes luminous. This result, however, is probably due to the formation of acetylene on the heated surface as well as to the increased temperature of the gas.

The present position of the theory of non-luminosity is that probably all three causes are operative.

Expt. 306.—The principle of the stability of the Bunsen flame, viz., that the combustible mixture of gas and air is passed up the tube more rapidly than the flame is propagated backwards through the mixture, may be illustrated by placing a long wide glass tube over a large Bunsen burner, and lighting the flame at the top (Fig. 360). On turning down the gas, the flame **strikes back,** *i.e.*, flashes down the tube. If the gas is turned down very slowly, the inner cone of the flame may be arrested halfway down the tube by a ring of copper wire hung inside, as shown. This prevents the propagation of the flame by cooling the gas below the ignition temperature.

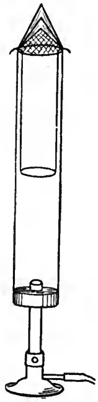


Fig. 360.—Separation of Cones of Bunsen Flame.

The detonation wave.—By measuring the speed of the mixture of gas and air or oxygen necessary to prevent the downward propagation of a flame in the apparatus described in Expt. 306, Bunsen (1867) found that the velocity of propagation of flame in a mixture of hydrogen and oxygen was 34 metres per sec. Later experiments by Berthelot, Mallard and Le Chatelier, and Dixon showed, however, that if the explosive mixture is fired at one end of a long tube, the flame, which at first traverses a short length of the tube with a velocity comparable with Bunsen's figure, rapidly increases in speed, and reaches a maximum, after which it flashes through the gas with a constant velocity very much higher than the initial velocity of the flame. This flame, travelling with the high constant speed, is called a **detonation wave.** The velocities of the detonation waves in various mixtures, determined by Dixon, are given below.

Gas.	**Velocity of detonation wave in m. per sec.**
$8H_2 + O_2$	3532
$2H_2 + O_2$	2821
$H_2 + 3O_2$	1707
$C_2N_2 + O_2$	2728
$H_2 + Cl_2$	1729

In some cases (*e.g.*, $C_2N_2 + O_2$) the velocity of the detonation wave is approximately that of the propagation of sound through the burnt gas heated to the temperature of combustion under the conditions of experiment: in others (*e.g.*, $2H_2 + O_2$) it is much higher than this.

The increased violence of the combustion, and the great speed of propagation of the flame, when the detonating wave has been established, may be demonstrated by the following experiments:

EXPT 307.—Fill two tubes with nitric oxide over water, one a large test-tube, and the other a strong tube 2 in. wide and 5 ft. long, closed at the ends with rubber bungs. Pour a few c.c. of carbon disulphide into each, and shake. Take out the stoppers, and ignite the gases with a taper. The mixture in each burns with a beautiful blue flame, but whilst that in the test-tube burns quietly away, the flame in the long tube runs down noiselessly until it approaches the middle, and then flashes down quickly, with a peculiar howling noise. In the long tube the detonation wave just begins. The lower part of the tube should be protected with a strong glass screen.

EXPT. 308.—A coil of lead piping, 30 ft. long and $\frac{1}{4}$ in. diameter, is fitted at each end with the ordinary brass coupling sockets used for gas connections. To one of these is attached, by a rubber washer, a thin glass test-tube, and to the other a strong glass tube with firing-wires sealed through the glass. The glass tube is fitted into the socket, by Faraday's cement, and also into a brass stopcock above (Fig. 361). The coil is filled with a mixture $2CO + O_2$, containing a little hydrogen, the test-tube fixed in place, and covered with a wire gauze cylinder. On passing a spark, the glass tube is shattered almost at the same instant as the flash is seen in the

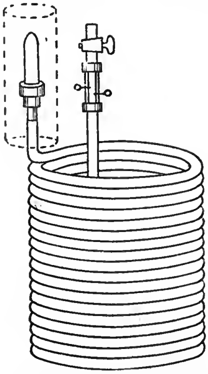


FIG. 361.—Velocity of Detonation Wave.

firing tube. The mixture $2CO + O_2$ burns in a test-tube without explosion.

EXERCISES ON CHAPTER XXXIV

1. How is carbon dioxide prepared, and what are its properties? How would you demonstrate (*a*) the gravimetric, (*b*) the volumetric, composition of the gas?

2. How has the atomic weight of carbon been determined?

3. How are percarbonates prepared? How has the composition of these substances been found? In what manner may a true percarbonate be distinguished from a carbonate containing H_2O_2 of crystallisation?

4. What is the carbon dioxide cycle in Nature? In what way is the composition of the atmosphere maintained approximately constant?

5. How is the amount of carbon dioxide in the air estimated? What is the normal proportion, and what effects have an excess of the gas on health? Compare the two oxides of carbon, CO and CO_2, as regards their poisonous properties.

6. In what ways do combustion and respiration resemble and differ from each other? How is the carbon dioxide content of the blood regulated?

7. How is carbon monoxide prepared? Under what conditions does the gas combine with (*a*) oxygen, (*b*) chlorine?

8. What reactions are supposed to occur in the burning of carbon? How may carbon monoxide be prepared from coke and oxygen?

9. What are the properties of carbon monoxide? Describe two experiments to illustrate the reducing properties of the gas.

10. How is carbon suboxide prepared, and what are its properties?

11. How are carbon disulphide and carbon oxysulphide prepared? What are the properties of these substances? What other sulphides of carbon have been described?

12. What are carbonyls?

13. Describe briefly the manufacture of producer gas, water gas, and carburetted water gas. How may hydrogen be obtained from water gas?

14. Describe the preparation and properties of cyanogen and hydrocyanic acid. How may (*a*) hydrocyanic acid, (*b*) carbon monoxide, be prepared from potassium ferrocyanide?

15. How are the following prepared: (*a*) potassium cyanate, (*b*) sodium thiocarbonate, (*c*) ammonium thiocyanate? What reaction takes place when a solution of ammonium cyanate is heated?

16. Describe experiments to illustrate the following: (*a*) flames are hollow, (*b*) the cause of luminosity of hydrocarbon flames, (*c*) the structure of the Bunsen flame.

17. What reactions are supposed to occur in the Bunsen flame? What evidence of these reactions may be offered?

18. To what causes is the loss of luminosity in the Bunsen flame ascribed? What experiments may be performed to support these theories?

19. What is a detonation wave? Describe experiments showing how such a wave is initiated.

CHAPTER XXXV

BORON AND SILICON

Boron and silicon.—Although **boron** and **silicon** belong to two different groups in the Periodic System, they show many analogies, and are conveniently studied together. Their general properties, in relation to the other elements of the groups in which they occur, will be considered at a later stage (pp. 890, 911).

BORON, B = 10·8.

Boron.—The salt **borax**, $Na_2B_4O_7,10H_2O$, has been known from very early times; it was brought from Tibet, and called *tincal*. Borax was used as a flux in metallurgy, and is mentioned by the Latin Geber. In 1702 Homberg obtained a crystalline substance by adding oil of vitriol to a solution of borax; from its medicinal properties this was known as *sal sedativum*. Baron (1747) showed that Homberg's "salt" must possess acidic properties, since, when it is treated with soda, borax is formed. It was therefore called **boracic acid,** or **boric acid,** and Lavoisier suggested that it consisted of oxygen united with a peculiar element, which he called boracium, or **boron**. Davy (1807) first obtained boron as an olive-brown powder by electrolysing moistened boric acid, or by heating fused boric acid (*i.e.*, **boron trioxide**, B_2O_3) with potassium. The preparation of boron by the second method was repeated on a larger scale by Gay-Lussac and Thenard (1808); they described the properties of the element.

Borax.—The greater part of the borax of commerce is prepared either from the natural borax of Lake Borax, in California, which contains a little more than one ounce of borax per gallon, or from minerals, such as:

Colemanite, $Ca_2B_6O_{11},5H_2O$, or $2CaO,3B_2O_3,5H_2O$, found in Asia Minor, and in America;
Boracite, $2Mg_3B_8O_{15},MgCl_2$, found at Stassfurt;
Borocalcite, $CaB_4O_7,4H_2O$;
Boronatrocalcite, $Na_2B_4O_7,Ca_2B_6O_{11},16H_2O$, found in South America.

In the preparation of borax, the minerals, such as colemanite, are ground to a fine powder and boiled with sodium carbonate solution (15 parts of mineral + 10 parts of Na_2CO_3 + 60 parts of water) for three hours :

$$2(2CaO,3B_2O_3) + 3Na_2CO_3 = 3CaCO_3 + CaO + 3Na_2B_4O_7.$$

The solution is filtered, and allowed to crystallise for three days in vats. The borax is drained, broken up, and packed in kegs.

Borax forms two important hydrates : **octahedral borax,** $Na_2B_4O_7,5H_2O$, is obtained by crystallisation from a warm solution, above 35·5° ; at lower temperatures the salt deposits as common, **monoclinic borax,** $Na_2B_4O_7,10H_2O$. The crystals, and powder, swell up considerably on heating, forming anhydrous borax, which fuses at a higher temperature to a transparent glass. Borax is slightly hydrolysed in solution, and since boric acid, H_3BO_3, is a very weak acid, the solution is alkaline : $Na_2B_4O_7 + 3H_2O \rightleftharpoons 2NaBO_2 + 2H_3BO_3$ (concentrated solutions) ; $NaBO_2 + 2H_2O \rightleftharpoons NaOH + H_3BO_3$ (dilute solutions). Borax is used in laundering for imparting a gloss to linen in ironing, and (on account of the properties of boric acid) as an antiseptic. Fused borax readily dissolves metallic oxides, often producing characteristic colours (**borax-bead reactions :** CuO, blue ; Cu_2O, red ; Cr_2O_3, green ; MnO_2, violet ; CoO, deep blue ; NiO, yellowish-brown ; FeO, green ; Fe_2O_3, brown). Borax is used in preparing glazes, as a flux in soldering, and in making optical and hard glass.

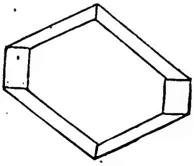


FIG. 362.—Crystal of Boric Acid.

Boric acid, H_3BO_3.—Boric acid is produced from borax by treating it with a mineral acid. It is sparingly soluble in cold water, but dissolves fairly easily in hot water. One hundred c.c. of water dissolve 1·95 gm. at 0°, 2·92 gm. at 12°, and 16·82 gm. at 100°.

EXPT. 309.—To a hot saturated solution of borax add concentrated hydrochloric acid till the solution is strongly acid to litmus. On cooling, scaly, six-sided, triclinic crystals of boric acid (Fig. 362) separate : $Na_2B_4O_7+2HCl+5H_2O=2NaCl+4H_3BO_3$. Wash the crystals with cold water, and recrystallise them from hot water.

In the volcanic regions of Tuscany, jets of steam, called *suffioni*, escape from the ground, and are surrounded by lagoons ; these jets contain steam, nitrogen, ammonia, and traces of boric acid, which is volatile in steam. The boric acid of *suffioni* has probably been produced by the action of superheated water on boron nitride : $BN + 3H_2O = H_3BO_3 + NH_3$. In the recovery of the boric acid, a basin is built around two or three of the *suffioni*, and the steam is condensed in water. The liquid is concentrated by the heat of the steam ; it passes through successive basins on a sloping hillside

(Fig. 363), and becomes enriched in boric acid. The liquid, containing about 2 per cent. of the acid, is then concentrated in flat lead pans by the heat of the steam, and the crystals of boric acid separating are recrystallised and dried.

Ordinary boric acid, or **orthoboric acid,** H_3BO_3, forms soft, silky, white crystals with a greasy feel. On heating to 100°, these lose water and form **metaboric acid,** HBO_2. At 140°, **pyroboric acid,** $H_2B_4O_7$, is said to be formed ; at a red heat the whole of the water is lost, with formation of **boric anhydride,** or **boron trioxide,** B_2O_3, which softens to a hygroscopic, glassy mass at a red heat :

$$4H_3BO_3 = 4HBO_2 + 4H_2O = H_2B_4O_7 + 5H_2O = 2B_2O_3 + 6H_2O.$$

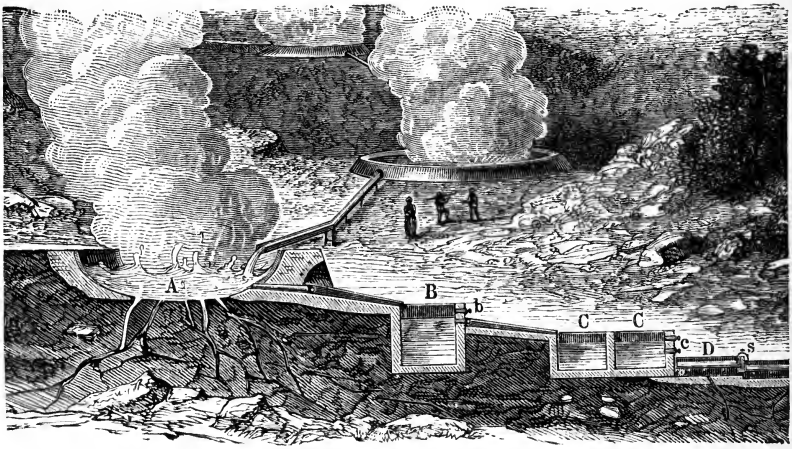
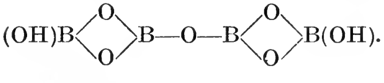


Fig. 363.—Boric Acid Lagoons.

The constitutional formulæ of the acids may be written: Orthoboric acid, $B(OH)_3$; metaboric acid, $O{:}B(OH)$; pyroboric acid,



Orthoborates are infrequent : magnesium borate, $Mg_3(BO_3)_2$, and ethyl borate, $B(OC_2H_5)_3$, are best known. **Metaborates** are the most stable, and pyroborates are also stable. Borax, or **sodium pyroborate,** $Na_2B_4O_7,10H_2O$, is formed by adding a solution of caustic soda, or sodium carbonate, to boric acid : since it contains twice as much boric anhydride, B_2O_3, as the normal salt, it is often called a **diborate** : $Na_2O,2B_2O_3$. Metallic borates, usually metaborates, are precipitated by adding a solution of borax to the metallic salts dissolved in water: $Na_2B_4O_7 + BaCl_2 + 3H_2O = Ba(BO_2)_2$ (**barium metaborate**) $+ 2H_3BO_3 + 2NaCl$. Metaborates are also formed in the borax-bead reaction: $Na_2B_4O_7 + CuO = Cu(BO_2)_2 + 2NaBO_2$.

Boron trioxide shows feebly basic properties as well as being the anhydride of the weak boric acid. Boric acid combines with sulphur trioxide, forming **boron hydrogen sulphate,** $B(HSO_4)_3$, and with phosphoric acid to produce **boron phosphate,** BPO_4, insoluble in water and dilute acids, but soluble in alkalies. In this respect, boron resembles aluminium (p. 896).

Boric acid is a very weak acid. It turns litmus a wine-red colour, but has no action on methyl-orange. It is weaker than carbonic acid, or even hydrogen sulphide, as is seen from the following table of the fractions ionised in 0·1 normal solutions at 18°:

	a		*a*
Hydrochloric acid	0·92	Carbonic acid ($H{\cdot}HCO_3$)	0·0017
Sulphuric acid	0·61	Hydrogen sulphide ($H{\cdot}HS$)	0·0007
Acetic acid	0·013	Boric acid ($H{\cdot}H_2BO_3$)	0·0001
		Hydrocyanic acid	0·0001

Boric acid ionises as a monobasic acid, and may be titrated with caustic soda after addition of excess of glycerin, with phenolphthalein as indicator: $H_3BO_3 + NaOH = NaBO_2 + 2H_2O$. Since the acid has no action on methyl-orange, a solution of borax may be titrated with this indicator as if it were a solution of caustic soda: $Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$.

Boron.—The element **boron** may be obtained by heating boron trioxide with potassium (Davy): $B_2O_3 + 6K = 2B + 3K_2O$. It is more conveniently prepared by heating potassium borofluoride (*q.v.*) with potassium: $KBF_4 + 3K = 4KF + B$, but the most convenient process is to heat boron trioxide with magnesium: $B_2O_3 + 3Mg = 2B + 3MgO$. The chestnut brown powder left on treating the mass with hydrochloric acid may be purified by treatment with hydrofluoric acid and fusion with B_2O_3 in a stream of hydrogen (Moissan, 1902).

EXPT. 310.—Heat 5 gm. of magnesium powder with 15 gm. of powdered boron trioxide in a covered crucible. When the violent reaction ceases, cool, and place the crucible in a beaker containing diluted hydrochloric acid (1 : 2). Filter and wash. In the later stages of the washing, observe that the boron begins to pass through the filter-paper in the form of a yellowish-brown **colloidal solution,** from which it is precipitated by acids and salts. Dry the boron in a steam oven.

Amorphous boron so prepared is a brown powder, sp. gr. 2·45; it is unaltered in air at the ordinary temperature, but smoulders at about 700°, with formation of the trioxide and **boron nitride,**

BN. These produce a superficial coating over the boron and prevent complete reaction. Boron displaces carbon and silicon from their oxides on heating: $3SiO_2 + 4B = 2B_2O_3 + 3Si$.

Moissan's boron, prepared as above, always contains oxygen, and is probably a solid solution of **boron suboxide,** B_4O_3, in boron. Weintraub (1909) states that pure boron is insoluble in 40 per cent. nitric acid, which dissolves a considerable proportion of Moissan's boron, leaving a residue of pure boron. **Pure boron** is obtained by striking an alternating current arc in a mixture of hydrogen and boron trichloride vapour, between water-cooled copper electrodes in a glass globe. The boron powder collecting on the electrodes fuses to globules, which drop off (Pring and Fielding, 1910). As so prepared, boron forms a black, very hard, solid with a conchoidal fracture, melting at 2200°, but volatilising appreciably at 1600°. It may be strongly heated in air without oxidation, and is only very slowly attacked by concentrated nitric acid. It thus differs in properties from Moissan's boron.

Boron is one of the few elements which combine directly with nitrogen (p. 540): the nitride is also produced by heating borax with ammonium chloride:

$$Na_2B_4O_7 + 4NH_4Cl = 4BN + 2NaCl + 2HCl + 7H_2O.$$

When boron is heated in nitric oxide it burns: $5B + 3NO = B_2O_3 + 3BN$. **Boron nitride,** BN, is a white infusible powder, unchanged by mineral acids, solutions of alkalies, or chlorine at a red heat. It is decomposed by fusion with potash, when heated in steam: $2BN + 3H_2O = B_2O_3 + 2NH_3$, or (slowly) by hydrofluoric acid: $BN + 4HF = NH_4BF_4$. When fused with potassium carbonate, it forms potassium cyanate: $BN + K_2CO_3 = KBO_2 + KCNO$.

Boron forms the **carbides,** BC and B_6C, on heating with carbon in the electric furnace, and a **sulphide,** B_2S_3, by direct combination at a white heat, or by heating B_2O_3 + carbon in the vapour of CS_2. The sulphide is hydrolysed by water: $B_2S_3 + 3H_2O = B_2O_3 + 3H_2S$. With H_2S, metathioboric acid, $H_2B_2S_4$, is formed. B_2S_5 is also known, formed from BI_3 and S dissolved in CS_2.

Crystalline boron was obtained by Deville and Wöhler (1856) by fusing boron with aluminium at 1300°. On cooling, crystals formed on the surface of the aluminium. The metal may be dissolved in hydrochloric acid, leaving crystals of *adamantine boron*—some clear and colourless, others brown, but all having the crystalline form of the diamond. Crystalline boron is very resistant to heat or acids, but dissolves in fused alkalies. The crystals always contain about 4 per cent. of carbon and up to 7 per cent. of aluminium, and are usually regarded as a definite compound, AlB_{12}, or $B_{48}C_2Al_3$. Graphite-like laminæ of AlB_{12} are also formed in Wöhler's process.

Boron hydrides.—If equal weights of boron trioxide and magnesium powder are heated, **magnesium boride** appears to be formed, since the residue, when treated with hydrochloric acid, evolves hydrogen with has a peculiar smell, and burns with a green-edged flame (Francis Jones, 1879). Ramsay and Hatfield (1901) showed that the gas, which was supposed to contain a tri-hydride BH_3, contains several hydrides, which may be condensed out in liquid air, but no BH_3. The investigations of Stock and his pupils since 1912 have shown that probably ten **hydrides of boron** exist ; a gas, B_2H_6, two volatile liquids, B_4H_{10} and B_6H_{12}, and several solid hydrides of doubtful formulæ. BH_3 does not exist.

The liquid condensed out of the gas from magnesium boride and hydrochloric acid by cooling in liquid air is a mixture of the two hydrides B_4H_{10} and B_6H_{12}, which can be separated by fractionation, the latter being less volatile. At the ordinary temperature, these hydrides are colourless liquids, boiling at 16° and about 100°, respectively. By heating B_4H_{10}, a colourless gas, B_2H_6, which forms a liquid boiling at $-87°$ and very stable when pure, is obtained. This reacts with water : $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$. It probably contains quadrivalent boron : $H_3B{\cdot}BH_3$. On heating B_2H_6, several **solid hydrides** are formed. One of these, $B_{10}H_{14}$, is volatile *in vacuo*, and soluble in alcohol, ether, and benzene. A colourless solid, possibly $B_{12}H$, is non-volatile but soluble in carbon disulphide, whilst a yellow solid, possibly B_5H_{14}, is non-volatile and insoluble in that solvent. By the action of B_2H_6 and B_4H_{10} on solutions of alkalies, unstable **hypoborates,** $RO{\cdot}BH_3$, are formed. By the action of chlorine on B_2H_6, the compound B_2H_5Cl is obtained.

Halogen compounds of boron.—The following **halogen compounds of boron** are known :

BF_3 ; colourless gas, condensing to colourless, mobile liquid, m.-pt. $-127°$, b.-pt. $-101°$.
BCl_3 ; colourless, mobile liquid, m.-pt. $-104°$, b.-pt. 12·5°. sp. gr. 1·4.
BBr_3 ; colourless, viscous liquid, m.-pt. $-46°$, b.-pt. 99°.
BI_3 ; white, leafy crystals, m.-pt. 43°, b.-pt. 210°.

Boron fluoride, BF_3, is obtained by the spontaneous combustion of boron in fluorine, or by heating a mixture of fluorspar, boron trioxide, and concentrated sulphuric acid in a lead retort :

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O.$$

The gas is collected over mercury. It fumes strongly in moist air, and when passed into water gives a precipitate of boric acid ; this redissolves if more gas is passed through, and the solution then contains **fluoboric acid,** HBF_4 : $4BF_3 + 3H_2O \rightleftharpoons B(OH)_3 + 3HBF_4$. The solution on distillation gives a strongly acid liquid of composition $BF_3,2H_2O$; in concentrated solutions BF_3 and HF are also present. The acid forms salts, **borofluorides,** *e.g.*, KBF_4. BF_3 readily combines with ammonia, giving a white solid, BF_3,NH_3, and liquids supposed to be $BF_3,2NH_3$ and $BF_3,3NH_3$. Borofluorides are formed in solution from boric acid and acid fluorides :

$$H_3BO_3 + 2NaHF_2 = NaBF_4 + NaOH + 2H_2O.$$

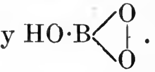
Boron chloride, BCl_3, is obtained by burning amorphous boron in chlorine, or by passing chlorine over a strongly-heated mixture of boron trioxide and charcoal: $B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO$. It is condensed in a freezing mixture.

Chlorine has an affinity for boron, and carbon for oxygen, but neither element alone can effect the decomposition of boron trioxide. The united action of the two affinities can, however, resolve the oxide.

Boron trichloride is also produced by heating B_2O_3 with phosphorus pentachloride in a sealed tube at 150°: $B_2O_3 + 3PCl_5 = 2BCl_3 + 3POCl_3$.

The liquid is freed from chlorine by distillation over mercury. It fumes strongly in moist air, and is immediately hydrolysed by water: $BCl_3 + 3H_2O = B(OH)_3 + 3HCl$; the reaction is not reversible (*cf.* p. 450). When passed into liquid ammonia at − 23° it forms **boron amide,** $B(NH_2)_3$; at 0° $B_2(NH)_3$, **boron imide,** is formed.

The **bromide,** BBr_3, is obtained by similar methods to the chloride; the **iodide,** BI_3, is formed by passing BCl_3 and HI through a heated tube.

Perborates.—If a mixture of boric acid and sodium peroxide is added to ice-cold water, a **perborate,** $Na_2B_4O_8,10H_2O$, is produced. On treating with hydrochloric acid, this forms a **meta-perborate,** $NaBO_3,4H_2O$. A salt, $Na_2B_4O_{11}$, is formed from H_2O_2, Na_2O_2, and pyroboric acid at 0°. These salts are stable in the solid state, but they decompose in solution with formation of hydrogen peroxide. They liberate iodine from iodides, and decolorise permanganate. Perborates are used in bleaching, and as antiseptics. The salts $2KBO_3,H_2O$ and $2KBO_3,H_2O_2$ are known. **Perboric acid** is given the formula O:BO·OH, or possibly  .

Tests for boric acid.—If a solution of a borate is acidified with hydrochloric acid, and a piece of **turmeric paper** dipped into the solution and dried, a brownish-red colour is produced, similar to that formed by alkalies. If the paper is now moistened with an alkali, it turns greenish-black.

Ethyl borate, $B(OC_2H_5)_3$, is formed when a borate is distilled with alcohol and concentrated sulphuric acid: $B(OH)_3 + 3C_2H_5OH \rightleftharpoons B(OC_2H_5)_3 + 3H_2O$. The vapour of this compound burns with a green flame.

EXPT. 311.—Add a little borax, and then concentrated sulphuric acid, to alcohol in a dish. Stir well and ignite. The flame is tinged green, especially if blown out and rekindled. Since copper and barium salts also colour the alcohol flame green, the test is most satisfactorily made by heating the mixture in a small flask fitted with a glass jet (Fig. 364), and burning the vapours after admixture with air in a wider tube to destroy the luminosity of the flame (due to ether, $(C_2H_5)_2O$, also formed).

Since boric acid interferes in qualitative analysis with the separation of the metals in Groups III, IV, and V (p. 630), and magnesium, it is removed, if its presence has been detected, by repeated evaporation of the solution with dilute hydrochloric acid. The boric acid is **volatile in steam,** and is slowly but completely eliminated. If the acid is not removed, insoluble borates, *e.g.*, calcium borate, $Ca(BO_2)_2$, are precipitated by ammonia in Group III.

Lower oxides of boron.—The oxide B_4O_3 is supposed to be contained in Moissan's amorphous boron. By decomposing magnesium boride with cold water, evaporating the filtered solution *in vacuo*, and heating, the oxide B_2O_2 is obtained (Travers, 1914). B_4O_5 is obtained by adding magnesium boride to water: $Mg_3B_2 + 6H_2O = Mg_3B_2(OH)_6 + 3H_2$, and treating the compound $Mg_3B_2(OH)_6$ with ammonia for several days in an atmosphere of hydrogen. The filtrate is evaporated to dryness *in vacuo*, when a pale brown solid, B_4O_5, is left. The magnesium compound derived from $B_2(OH_2)_6$ has been called a **borohydrate,** by analogy with carbohydrates. The solution also contains small quantities of compounds which evolve hydrogen with acids, possibly borohydrates, of the formulæ $H_6B_2O_2$ and $H_6B_2O_3Mg$, in which boron is quinquevalent. (Travers, Ray, and Gupta, 1912.)

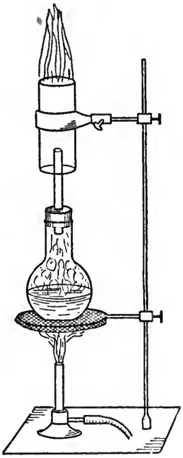


FIG. 364.—Green Flame of Ethyl Borate.

SILICON, Si = 28·1.

Silica.—Next to oxygen, **silicon** is the most abundant element in the crust of the earth (p. 32): it occurs in combination with oxygen as **silicon dioxide,** or **silica,** SiO_2, varieties of which are quartz, sand, flint, etc. Silica is also the acidic constituent of the very abundant *silicate rocks*. Granite and similar primitive rocks contain from 20 to 30 per cent. of silicon. Silica was at first regarded as an "earth," analogous to lime and alumina, but its acidic character was pointed out by Otto Tachenius in 1668: it is insoluble in acids, but dissolves in potash, forming a solution of a silicate, formerly known as *liquor of flints*. Tachenius also observed that acids differ in strength; one acid is displaced from its compounds by a stronger acid. The acidic character of silica explains the formation of *slags* in metallurgical operations. These are glassy or stony masses formed in smelting ores containing silica or silicates, to which lime has been added, and consist principally of the silicates of calcium and aluminium.

Lavoisier, who included silica among the earths, expressed the opinion that the latter " must soon cease to be considered as simple bodies," and are probably " compounds consisting of simple substances, perhaps metallic, oxydated to a certain degree." Gay-Lussac and Thenard in 1801 obtained a brown amorphous powder on passing the vapour of silicon chloride over heated potassium; this was **silicon**, the element of which silica is the oxide, but its true character was not elucidated by the French chemists. In 1823 Berzelius prepared silicon by heating potassium silicofluoride with potassium: $K_2SiF_6 + 4K = 6KF + Si$. He considered it to be a metal—*silicium*—whereas Davy, from its analogy with carbon, regarded it as a non-metal. In most of its properties silicon belongs to the group of non-metallic elements, although it forms alloys with metals, such as copper and iron. It differs from carbon, which also forms alloys, by giving a solid, difficultly-fusible dioxide, SiO_2, which is the chemical analogue of carbon dioxide, CO_2. The remaining compounds of silicon, however, resemble more closely those of carbon:

Carbon tetrachloride, CCl_4, b.-pt. 76°; **silicon tetrachloride,** $SiCl_4$, b.-pt. 57°.

Chloroform $CHCl_3$, b.-pt. 60°; **silicon chloroform,** $SiHCl_3$, b.-pt. 34°.

The great difference in physical properties between silica and carbon dioxide would therefore seem to be due rather to some peculiarity of silica itself than to the element silicon. Probably it has its foundation in the highly polymerised nature of the molecule of silica, $(SiO_2)_n$, since substances of high molecular weight usually have high boiling points (*cf.* H_2S and H_2O, p. 482). This is confirmed by the examination of quartz by the X-rays (p. 1018).

The forms of silica.—Silica occurs both *crystallised* and *amorphous.* Three main crystalline forms have been described, viz., *quartz, tridymite,* and *cristobalite,* although two forms of each are said to exist having definite transition points (Fenner, 1912):

α-**quartz** (tetartohedral hexagonal) $\overset{575°}{\rightleftharpoons}$ β-**quartz** (hemihedral hexagonal).

β-**quartz** $\overset{870° \pm 10°}{\rightleftharpoons}$ β-**tridymite** (holohedral hexagonal),

β-**tridymite** $\overset{1470° \pm 10°}{\rightleftharpoons}$ β-**cristobalite** (cubic).

By rapidly cooling β-tridymite and β-cristobalite, they pass at the following temperatures into metastable forms with a lower optical symmetry (p. 434):

β-**tridymite** $\overset{115°-120°}{\rightleftharpoons}$ α-**tridymite** (biaxial, perhaps orthorhombic),

β-**cristobalite** $\overset{180°-270°}{\rightleftharpoons}$ α-**cristobalite** (biaxial).

Silica occurs not only in the mineral kingdom, but also as a constituent of vegetable and animal organisms. The straw of cereals and the bamboo cane contain it in fairly large quantities: the common weed "horse-tail" leaves on combustion a siliceous skeleton. The feathers of some birds contain 40 per cent. of silica, which also occurs in sponges, and vast deposits of almost pure silica are found at Hanover, near Berlin, and in other localities, in the form of *kieselguhr*, which consists of the siliceous skeletons of extinct *diatoms*. This material, being very porous, is used to absorb nitroglycerin in the preparation of dynamite, and in lagging steam pipes to retard loss of heat.

Superheated water in the interior of the earth, especially if alkaline, dissolves silica: the latter occurs in many spring waters, in hot-springs (Black, 1794), and particularly in the boiling water of geysers, such as the Great Geyser of Iceland, the Hot Springs of New Zealand, and the Mammoth Springs of Yellowstone Park, U.S.A. The dissolved silica is deposited in the hydrated form at the mouth of the geyser, as *sinter*. It may also pass into the pores of wood, etc., in the earth, producing *petrifaction*.

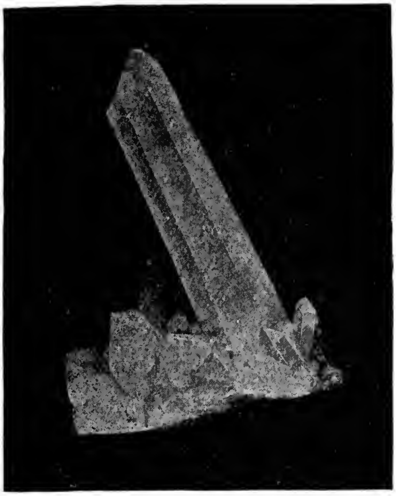


FIG. 365.—Crystals of Quartz.

Quartz.—*Quartz* (sp. gr. 2·66), or *rock-crystal*, formerly believed to be "a hard form of ice," occurs sometimes in clear, colourless crystals (Figs. 365–6) used for the preparation of spectacle lenses ("pebbles"), prisms, and optical apparatus, but is more frequently found in opaque ("milky") or coloured masses ("smoky-quartz," "cairngorm"): coloured varieties of quartz (*e.g.*, purple, in *amethysts*) are used as gems. *Sand* consists of quartz, which remains unchanged after the disintegration, or "weathering," of rocks, and has been crushed during its movement by water.

The purest forms of sand are white ("Calais sand"); yellow sand is coloured by ferric oxide, much of which may be dissolved by boiling with hydrochloric acid. Clay may also be present. *Sandstone* consists of sand grains cemented together, with oxide of iron, or other materials.

"Singing sand," which emits a peculiar squeaking note when pressed, consists of rounded grains of nearly uniform size. It occurs in patches along with ordinary sand in various localities—*e.g.*, near Poole.

The **crystalline form of quartz** is somewhat complicated; it is apparently that of the hexagonal prism, terminated by the hexagonal pyramid, but really belongs to the trigonal system of symmetry, and possesses optical activity of a peculiar kind. Some crystals exhibit hemihedral faces (p. 440) inclined to the right, others to the left, so that one type of crystal is the mirror-image of the other (Fig. 367). Such pairs of crystals are known as **enantiomorphs,** and they are said to show the crystallographic phenomenon of **enantiomorphism.** This two-sided character of the outer form has its counterpart in the internal structure of the crystal, as exhibited by its optical properties: right-handed, or *dextrogyrous*, quartz crystals rotate the plane of polarised light to the right, left-handed, or *lœvogyrous* quartz crystals rotate the plane of polarisation to the left. The rotation is proportional to the thickness of crystal traversed.

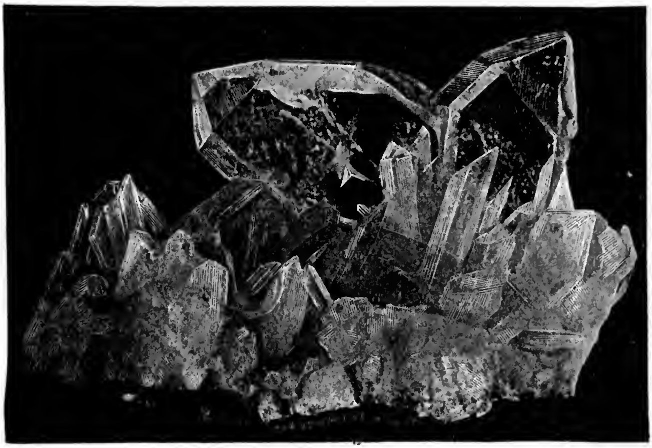


FIG. 366.—Crystals of Quartz (British Museum).

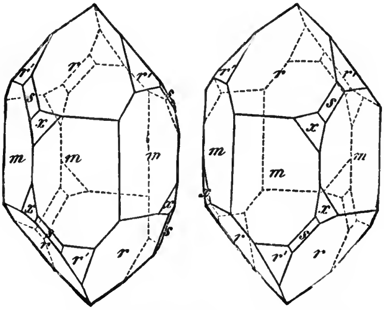


FIG. 367.—Enantiomorphous Crystals of Quartz.

Tridymite.—**Tridymite** (sp. gr. 2·30) occurs more rarely than quartz, in minute crystals, usually in the form of six-sided plates

(Fig. 368), in cavities in the trachytic rocks of Mexico, and Stenzelborg. It belongs to the triclinic system.

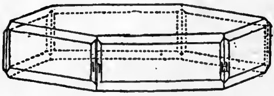


FIG. 368.—Crystalline Form of Tridymite.

Quartz and tridymite appear to have been deposited from solution. If hydrated silica (p. 744) is heated with a solution of soluble glass (sodium silicate) in a sealed glass tube, small crystals of quartz are formed. A solution of soluble glass alone dissolves part of the glass tube, and on cooling silica is deposited; above 180° quartz is formed, at lower temperatures tridymite, and at the ordinary temperature amorphous silica. Larger crystals of quartz are produced by the prolonged heating at 250°, in a sealed tube, of a 10 per cent. solution of colloidal silica.

Cristobalite.—This crystalline variety, discovered by Schwarz (1912), is obtained by heating powdered amorphous (fused) quartz to 1500°. It has a specific gravity of 2·519.

Amorphous silica.—All the varieties of silica fuse in the oxy-hydrogen blowpipe at about 1625°, and boil in the electric furnace at 1700–1750°. They become plastic before fusion, and may be worked and blown like glass, or drawn into thread. The amorphous, vitreous product, called *quartz glass*, has a very small coefficient of expansion (cubical coefficient $= 10^{-7}$), and may therefore be heated to redness and quenched in cold water without fracture. It is transparent to the ultra-violet rays, whilst ordinary glass is opaque.

Besides the transparent silica obtained by fusion, a translucent variety, known as *vitreosil*, is manufactured by fritting sand with an electrically-heated carbon rod or plate, previously wrapped in paper, which when carbonised prevents the fused silica from sticking to the carbon heater.

Amorphous silica occurs in Nature in a variety of forms. Masses of **quartz** are apparently amorphous, and break with a conchoidal fracture, but probably have a fine (*cryptocrystalline*) crystalline structure. Mixtures of amorphous silica with quartz or tridymite occur as **chalcedony,** which is translucent and yellow (sp. gr. 2·3); other varieties are the gems **carnelian** (red), **sard** (brown-red), **chrysoprase** (apple-green), **onyx,** and **sardonyx** (red). Common **flint** occurs in rounded nodules in chalk ("chert"), coloured yellow, grey or black by oxide of iron. It is very hard, and splits with a conchoidal fracture, giving sharp edges—hence its use in the "Stone Age." The **opal** (sp. gr. 2·2) contains 2–13 per cent. of water, and has, like other amorphous varieties, apparently been formed by the drying of colloidal silica (*q.v.*). The *noble* or *gem opal* shows brilliant colours by the interference of light in thin layers. *Waxy opal* is found in large quantities in Queensland.

Mixtures of the above forms with crystalline quartz and tridymite occur. Crystals of tridymite are often left on treating opal with caustic potash. **Agates**, used in making mortars, are mixtures of opal or chalcedony with quartz or tridymite, and have a banded structure, which seems to indicate that they have been deposited in layers from water on the sides of a " pipe." The **cat's eye** consists of crystals of quartz enclosing fibres of asbestos. **Jasper** is opal deposited in layers of various colours.

Pure silica occurs as transparent rock-crystal, or may be obtained in the amorphous form from mineral silicates by fusing the finely-powdered mineral with excess of a mixture of potassium and sodium carbonates in a platinum crucible until evolution of carbon dioxide ceases. Alkali silicates (*e.g.*, sodium metasilicate, Na_2SiO_3) are formed: $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$. Commercial sodium silicate has approximately the composition $Na_2O,4SiO_2$. The residue on cooling is powdered and boiled with hydrochloric acid, which dissolves impurities, such as oxide of iron, and precipitates **gelatinous silica**, a hydrated form. The whole is evaporated to dryness on a water-bath. The silica then becomes granular and quite insoluble in water. It is washed with boiling hydrochloric acid until quite free from iron, then with boiling water till free from acid and alkali-chlorides, and is finally heated to redness in a platinum dish. It forms an impalpable white powder, insoluble in water and all acids except phosphoric and hydrofluoric. It dissolves in hot concentrated caustic alkalies.

The above process serves for the detection and estimation of silica in minerals, and manufactured products. A simple qualitative test is to heat a fragment of the mineral in a microcosmic bead (p. 633). All metallic oxides dissolve in the sodium metaphosphate, and a skeleton of silica is left floating in the bead. A sodium carbonate bead dissolves silica with effervescence, and remains clear on cooling: sodium silicate is formed.

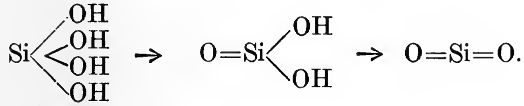
At high temperatures, silica, being a practically non-volatile acidic oxide, is able to displace volatile acids from their salts. If heated with sodium sulphate it drives out the volatile sulphur trioxide: $Na_2SO_4 + SiO_2 = Na_2SiO_3 + SO_3$. It is, however, relatively inert and refractory, and is used for making *refractory bricks* (ganister, Dinas brick, etc.) for furnace-linings. For this purpose pure sand, or crushed quartz-rock, is mixed with a little lime and clay, and old broken firebrick (" grog "); the mass is moistened, moulded, and burnt.

Silicic acids.—Gelatinous silica, freshly precipitated by the addition of acids to solutions of sodium or potassium silicates, is appreciably soluble in water, alkali, sodium carbonate, and acids.

When dried in the air, it retains about 16 per cent. of water, corresponding roughly with the formula, SiO_2,H_2O or H_2SiO_3, of **meta-silicic acid.** At 100°, 13 per cent. of water remains, and the silica is then insoluble. On further heating, water is gradually lost, but the vapour-pressure curve shows no breaks indicative of hydrates (p. 204). If water-vapour is readmitted to the partially dehydrated mass, it is reabsorbed, but the pressure is higher than in the corresponding part of the dehydration curve. At about 500° all the water is lost. The hydrated form of silica precipitated when silicon fluoride or chloride is decomposed by water (p. 752) is often assumed to be **orthosilicic acid,** $Si(OH)_4$; it has this composition when washed rapidly with benzene and ether and dried between filter-paper at the atmospheric temperature, but the existence of $Si(OH)_4$ is doubtful. The relations between the ortho- and meta-acids and the anhydride would be as follows:

$$Si(OH)_4 \xrightarrow{-H_2O} SiO(OH)_2 \xrightarrow{-H_2O} SiO_2$$

or



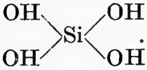
Colloidal silica.—If a dilute solution of sodium silicate is poured slowly, with stirring, into an excess of dilute hydrochloric acid, no precipitation of silica occurs, although the reaction $Na_2SiO_3 + 2HCl = 2NaCl + (SiO_2 + H_2O)$ has taken place, as may be shown by the diminution in electrical conductivity consequent upon the disappearance of the hydrogen ions. If the liquid be poured on a dialyser (p. 314), the sodium and chloride ions diffuse out, leaving a clear **colloidal solution,** or **hydrosol,** of **silicic acid** (p. 316). This was discovered by Graham in 1861. The colloidal solution may be concentrated by boiling in a flask to a certain extent, and by further evaporation over sulphuric acid until it contains 14 per cent. of SiO_2; it is then a clear, tasteless liquid with a feebly acid reaction. It is readily coagulated to a bluish-white, nearly transparent, jelly, the **hydrogel of silicic acid.** This, when washed with 90 per cent. alcohol, has approximately the composition H_2SiO_3. The hydrosol is more stable if small amounts of hydrochloric acid or caustic soda are added, but is at once coagulated by sodium carbonate or phosphate.

The silicates.—Although silicon does not form such a large number of compounds as the element carbon, the **silicates** enter into the composition of an extensive series of *rock-forming minerals,* the formulæ of which are often rather complex. Most silicates, however, may be regarded as salts of **six hypothetical silicic acids,** viz., orthosilicic acid, $Si(OH)_4$, and acids produced from one or more molecules of this by elimination of water.

Many mineral silicates have been prepared artificially.

1. H_4SiO_4 : **orthosilicic acid.**
2. $H_4SiO_4 - H_2O = H_2SiO_3$: **metasilicic acid.**
3. $2H_4SiO_4 - H_2O = H_6Si_2O_7(2SiO_2,3H_2O)$: **orthodisilicic acid.**
4. $2H_4SiO_4 - 3H_2O = H_2Si_2O_5(2SiO_2,H_2O)$: **metadisilicic acid.**
5. $3H_4SiO_4 - 2H_2O = H_8Si_3O_{10}(3SiO_2,4H_2O)$: **orthotrisilicic acid.**
6. $3H_4SiO_4 - 4H_2O = H_4Si_3O_8(3SiO_2,2H_2O)$: **metatrisilicic acid.**

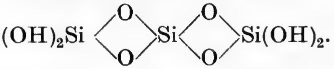
Structural formulæ of these acids may easily be derived, but are purely speculative :

1. H_4SiO_4 

2. H_2SiO_3 $SiO(OH)_2$.

3. $H_6Si_2O_7$ $(OH)_3Si-O-Si(OH)_3$. 4. $H_2Si_2O_5$ $OH{\cdot}O{\cdot}Si-O-Si{\cdot}O{\cdot}OH$.

5. $H_8Si_3O_{10}$ $(OH)_3Si-O-Si(OH)_2-O-Si(OH)_3$.

6. $H_4Si_3O_8$ 

Esters of ortho- and meta-silicic acids, with known molecular weights, have been prepared : $Si(OEt)_4$, $SiO(OEt)_2$.

Examples of silicates occurring in rocks, belonging to the six classes, are given below :

1. **Orthosilicates** : *zircon,* $ZrSiO_4$; *olivine,* Mg_2SiO_4 ; *garnet,* $Ca_3Al_2(SiO_4)_3$; *willemite,* Zn_2SiO_4 ; *potash mica,* $KH_2Al_3(SiO_4)_3$.
2. **Metasilicates** : *wollastonite,* $CaSiO_3$; *leucite,* $KAl(SiO_3)_2$; *beryl,* $Be_3Al_2(SiO_3)_6$; *enstatite,* $MgSiO_3$; *talc,* $H_2Mg_3(SiO_3)_4$; *asbestos,* $Mg_3Ca(SiO_3)_4$.
3. **Orthodisilicates** : *barysilite,* $Pb_3Si_2O_7$; *serpentine,* $Mg_3Si_2O_7 + 2H_2O$; *kaolinite,* $Al_2Si_2O_7 + 2H_2O$.
4. **Metadisilicates** : *millerite,* $Al_2HKCa_2(Si_2O_5)_6$; *petalite,* $LiAl(Si_2O_5)_2$.
5. **Orthotrisilicate** : *melilith,* $Ca_4Si_3O_{10}$.
6. **Metatrisilicates** : *orthoclase,* $KAlSi_3O_8$ *albite,* $NaAlSi_3O_8$.

Silicates not comprised in these six groups are usually considered as basic salts : *e.g., cyanite,* $(AlO)_2SiO_3$; *andalusite,* $Al(AlO)SiO_4$.

EXAMPLE.—Calculate the formula of the mineral silicate of the following composition :

SiO_2	$45{\cdot}07 \div 60{\cdot}4 = 0{\cdot}746$	6
Al_2O_3	$38{\cdot}41 \div 102{\cdot}3 = 0{\cdot}375$	3
K_2O	$12{\cdot}10 \div 94{\cdot}3 = 0{\cdot}128$	1
H_2O	$4{\cdot}42 \div 18 = 0{\cdot}245$	2

The formula is therefore $6SiO_2,3Al_2O_3,K_2O,2H_2O$, or $Si_3O_{12}Al_3KH_2$, or $Al_3KH_2(SiO_4)_3$, an **orthosilicate.**

Silicon.—Silicon has a great affinity for oxygen, so that the direct reduction of silica can be effected only by the use of powerful reducing agents, or at high temperatures. Silica is reduced when heated with carbon in the electric furnace, and **silicon** is manufactured in this way at Niagara by heating a mixture of sand and crushed coke in the proportions for the reaction: $SiO_2 + 2C = 2CO + Si$, or by reducing silica with calcium carbide. It is obtained as a hard grey crystalline mass, with the appearance and electric conductivity of graphite, and is used in the preparation of alloys (silicon-bronze; manganese-silicon-bronze), on which it confers the properties of hardness and tensile strength. Silica is also reduced when heated with carbon and iron in the blast furnace, and cast iron, therefore, always contains silicon. Iron containing carbon and more than 15 per cent. of silicon is very resistant to the action of acids.

In the laboratory, silicon is most conveniently prepared by heating silica with magnesium powder: $SiO_2 + 2Mg = 2MgO + Si$.

EXPT. 312.—A mixture of powdered quartz, or *thoroughly dried* amorphous silica, with the requisite amount of magnesium powder and one-fourth the weight of calcined magnesia to moderate the reaction, is carefully heated in a covered porcelain crucible. The mass glows when reaction occurs. After cooling, the magnesia is dissolved out by hydrochloric acid, and the silicon washed in a platinum dish with hydrofluoric and sulphuric acids to remove silica. It has a purity of 96–97 per cent. If washed on a filter, it begins to form a colloidal solution, as in the case of boron (p. 735).

Amorphous silicon, prepared by the above process, is a dark brown hygroscopic powder, sp. gr. 2·35, which burns brilliantly when heated to dull redness in oxygen. When heated in air, it burns superficially. It ignites spontaneously in fluorine, forming the fluoride, SiF_4, and burns when heated in chlorine, with production of the tetrachloride, $SiCl_4$. Amorphous silicon is insoluble in water and all acids except hydrofluoric; it is slowly attacked by steam at a red heat: $Si + 2H_2O = SiO_2 + 2H_2$. A mixture of potassium chlorate and nitric acid has no action upon it (*cf.* carbon), but it dissolves readily in concentrated caustic alkalies (*cf.* p. 183), or when fused with sodium carbonate, potassium nitrate, or potassium chlorate: $Si + 2KOH + H_2O = K_2SiO_3 + 2H_2$.

When amorphous silicon is strongly heated in a closed crucible, it fuses, and on cooling solidifies to the dense crystalline **graphitoidal silicon,** which also results from the reduction of silica in the electric furnace. **Octahedral crystals** of silicon, orange or black in colour, are produced by strongly heating potassium silicofluoride, K_2SiF_6, with zinc or aluminium in an iron crucible, and treating the mass with acid: $3K_2SiF_6 + 4Al = 4AlF_3 + 3Si + 6KF$. Zinc gives long needle-shaped crystals (**adamantine silicon**); aluminium, six-sided plates (**graphitoidal silicon**); both varieties are made up of regular octahedra. Crystalline silicon has a density of 2·49; it does not burn in oxygen, even when strongly heated, but burns in chlorine, and ignites in fluorine. When very strongly heated, it forms grey nodules of sp. gr. 3·0. It is attacked by a mixture of nitric and hydrofluoric acids, or by fusion with alkali: $Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$. When fused with sodium carbonate, it displaces carbon: $Si + Na_2CO_3 = Na_2SiO_3 + C$. Another variety (sp. gr. 2·42) appears to be formed on crystallising from molten silver. It is insoluble in hydrofluoric acid.

Silicon hydrides.—Silicon and hydrogen combine partly at the temperature of the electric arc, forming **silicon hydride,** SiH_4, **silico-methane,** or **monosilane**: $Si + 2H_2 \rightleftarrows SiH_4$. If magnesium powder and amorphous silica, in the proportions of 2 : 1 by weight, are heated in a crucible, **magnesium silicide,** which probably consists mainly of Mg_2Si, is formed as a blue crystalline mass. This, when treated with dilute hydrochloric acid in a flask from which air has been displaced by hydrogen, evolves a gaseous mixture of silicon hydrides with hydrogen, which is spontaneously inflammable: $Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$ (Buff and Wöhler, 1857). If the gas is bubbled through water, each bubble ignites in contact with the air, and burns with a luminous flame, producing a vortex ring of finely-divided silica: $SiH_4 + 2O_2 = SiO_2 + 2H_2O$ (*cf.* phosphoretted hydrogen).

If the gas, after washing with water and drying with calcium chloride and phosphorus pentoxide, is passed through a tube cooled in liquid air, a mixture of hydrides of silicon is condensed, and from the liquid, by fractionation, the following compounds may be isolated:

1. **Monosilane,** SiH_4, m.-pt. $-185°$, b.-pt. $-112°$, a colourless gas, stable at the ordinary temperature, spontaneously inflammable if mixed with the other hydrides, and sometimes if pure. The relative density is 16·02. It is decomposed when passed through a red-hot tube, yielding twice its volume of hydrogen: $SiH_4 = Si + 2H_2$. By the action of caustic alkalies, four times the volume of hydrogen is produced: $SiH_4 + 2KOH + H_2O = K_2SiO_3 + 4H_2$. The gas precipitates copper silicide, Cu_2Si, from copper salts, and silver from silver salts: $4AgNO_3 + SiH_4 = Si + 4Ag + 4HNO_3$.

Pure monosilane is obtained by heating **triethyl silico-formate** with sodium: $4SiH(OC_2H_5)_3 = SiH_4 + 3Si(OC_2H_5)_4$ (**ethyl orthosilicate**). The triethyl silico-formate (which is the silicon analogue of orthoformic ester, $CH(OC_2H_5)_3$) is obtained by the action of silicon chloroform on absolute alcohol, or sodium ethoxide, $NaOC_5H_5$:

$$SiHCl_3 + 3C_2H_5{\cdot}OH = SiH(OC_2H_5)_3 + 3HCl.$$

2. **Disilane,** Si_2H_6 **(silicon-ethane),** which is also formed by the action of concentrated hydrochloric acid on lithium silicide : $Li_6Si_2 + 6HCl = 6LiCl + Si_2H_6$, is a colourless gas, b.-pt. − 15°, m.-pt. − 132·5°, which is stable at the ordinary temperature, but rapidly decomposes at 300°. Its relative density is 31·7. Disilane inflames in the air, is soluble in benzene and carbon disulphide, and is decomposed by alkalies : $Si_2H_6 + 2H_2O + 4KOH = 2K_2SiO_3 + 7H_2$.

3. **Trisilane,** Si_3H_8, is a colourless liquid, b.-pt. 53°, m.-pt. − 117°, decomposing spontaneously at the ordinary temperature. Si_3H_8 and Si_2H_6 react vigorously with carbon tetrachloride and chloroform : $2CCl_4 + Si_2H_6 = 2SiCl_4 + 2C + 3H_2$.

4. **Tetrasilane,** Si_4H_{10}, b.-pt. 80–90°, m.-pt. − 93·5°, is less stable than Si_3H_8.

5. **Solid hydrides,** probably Si_5H_{12} and Si_6H_{14}, remain after fractionation.

The existence of **silicon-acetylene,** Si_2H_2, said to be formed as a yellow solid by the action of hydrochloric acid on calcium silicide, is doubtful. It has been stated to be $H_3Si_3O_2$, **silicone,** which on exposure to sunlight gives off hydrogen and leaves black Si_3O_2.

By the action of silane on solid bromine at − 80°, the substitution products SiH_3Br (m.-pt. − 94°, b.-pt. 1·9°) and SiH_2Br_2 (m.-pt. − 70·1°, b.-pt. 66°) are formed. By the action of water on SiH_3Br a colourless, odourless, combustible gas, **disiloxane,** $(SiH_3)_2O$, m.-pt. − 144°, b.-pt. − 15·2°, is produced.

Halogen compounds of silicon.—Compounds of silicon, of the types SiX_4 and $SiHX_3$, with all the halogens are known ; isolated compounds of the types SiH_2X_2 and SiH_3X have been prepared. A number of chlorides not corresponding with the type SiX_4 are also known, *e.g.*, Si_2Cl_6, Si_3Cl_8, Si_4Cl_{10}, Si_5Cl_{12}, Si_6Cl_{14}.

Silicon tetrachloride, $SiCl_4$.—This compound (Berzelius, 1823) is produced when amorphous silicon, or the mixture of this with magnesia obtained by heating 40 gm. of dry powdered sand with 10 gm. of magnesium powder, is heated in a current of dry chlorine : $Si + 2Cl_2 = SiCl_4$. Chlorine may also be passed over heated silicon-iron. An older method of preparation is to heat an intimate mixture of silica and carbon to whiteness in a porcelain tube in a stream of chlorine : $SiCl_4 \leftarrow \boxed{2Cl_2 + Si}\boxed{O_2 + 2C} \rightarrow 2CO$. The products of reaction are cooled in a worm-tube, when silicon tetrachloride condenses as a colourless volatile liquid, sp. gr. 1·524, m.-pt. − 89°, b.-pt. 56·9°, which fumes strongly in moist air owing to hydrolysis : $SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl$. When the gas is passed into water, gelatinous silica is deposited. Silicon tetrachloride combines with gaseous ammonia, forming a white amorphous solid, $SiCl_4,6NH_3$.

By the action of chlorine on silicon, besides $SiCl_4$, two other chlorides are formed: the **trichloride,** Si_2Cl_6 (b.-pt. 147°), and the **octachloride** (b.-pt. 210–215°). These may be separated by fractionation. The **trichloride,** Si_2Cl_6, is also produced when the vapour of the tetrachloride is passed over strongly-heated silicon. It is a colourless, fuming liquid, b.-pt. 147°, m.-pt. $-1°$, the hot vapour of which ignites spontaneously in the air. With water, it produces an explosive white solid, $Si_2H_2O_4$, or $(SiO{\cdot}OH)_2$, **silicon-oxalic acid:** $Si_2Cl_6 + 4H_2O = (SiO_2H)_2 + 6HCl$. The **octachloride,** Si_3Cl_8, forms with water a white powder, $H_4Si_3O_6$, **silicon-mesooxalic acid,** the structural formula of which has been given as $O{:}Si(OH){-}Si(OH)_2{-}(OH)Si{:}O$.

According to Troost and Hautefeuille, Si_2Cl_6 vapour begins to decompose at 350°, and is completely dissociated at 800°: $2Si_2Cl_6 \rightleftarrows 3SiCl_4 + Si$. At high temperatures (1000°) reaction begins in the reverse direction, and the vapour is stable. At lower temperatures, apparently, silicon does not react appreciably with $SiCl_4$.

The **bromides** $SiBr_4$ (b.-pt. 153°) and Si_2Br_6 (solid) are formed in the same way as $SiCl_4$, and by the action of bromine on Si_2I_6, respectively.

The **tetraiodide** SiI_4 is formed from iodine vapour and silicon. When heated with finely-divided silver at 280°, it forms the **tri-iodide** by a reaction of condensation: $2SiI_4 + 2Ag = 2AgI + Si_2I_6$. The tri-iodide forms splendid crystals, fuming in moist air. Si_3Br_8 and Si_4Br_{10} are formed by the action of the silent discharge on silicon-bromoform, $SiHBr_3$.

Six **oxychlorides** of silicon are said to exist. Si_2OCl_6 (b.-pt. 137°) is formed on passing $SiCl_4$ vapour over white-hot felspar. If the vapour of this, mixed with oxygen, is passed through a heated glass tube, the compounds $Si_4O_4Cl_8$ (b.-pt. 200°), $Si_4O_3Cl_{10}$ (b.-pt. 153°), $Si_8O_{10}Cl_{12}$ (b.-pt. about 300°), $Si_2O_3Cl_2$ (?, b.-pt. above 400°), and $Si_4O_7Cl_2$ (solid at 400°) are stated to be formed, separable by fractionation.

Silicon chloroform, $SiHCl_3$, b.-pt. 33°, m.-pt. $-134°$, sp. gr. 1·3438 (*cf.* chloroform, $CHCl_3$), discovered by Buff and Wöhler, is prepared by passing hydrogen chloride over silicon (or the mixture of silicon and magnesia, p. 747) at a dull red heat: $Si + 3HCl = SiHCl_3 + H_2$. The liquid condensed in a freezing mixture is fractionated to separate the silicon tetrachloride (b.-pt. 56·9°) also produced. Silicon chloroform is a colourless, mobile, fuming liquid, which is very inflammable and burns with a green-edged flame, emitting white fumes of silica. A mixture of the vapour with air or oxygen explodes when brought in contact with a flame. At 800° the vapour decomposes: $4SiHCl_3 \rightleftarrows 3SiCl_4 + Si + 2H_2$.

By the action of ice-cold water on silicon chloroform, **orthosilicoformic acid,** or **leucone,** $SiH(OH)_3$, is formed, which readily loses water by two molecules condensing to give **silicoformic anhydride,** $H_2Si_2O_3$.

This is a powerful reducing agent (*cf.* formic acid): $H_2Si_2O_3 + O_2 = 2SiO_2 + H_2O$ (*cf.* $H{\cdot}CO_2H + O = CO_2 + H_2O$). It is readily decomposed by dilute alkalies, with evolution of hydrogen: $H_2Si_2O_3 + H_2O = 2SiO_2 + 2H_2$. On heating, silicoformic anhydride decomposes ultimately into silica, silicon, and hydrogen: $2H_2Si_2O_3 = SiH_4 + 3SiO_2 = Si + 2H_2 + 3SiO_2$.

Silicon bromoform, $SiHBr_3$ (b.-pt. 116°, m.-pt. $< -60°$), is formed by the action of hydrogen bromide on silicon; **silicon iodoform,** $SiHI_3$ (b.-pt. *c.* 220°), is formed by the action of a mixture of hydrogen iodide and iodine on silicon. Numerous mixed halogen compounds of silicon, *e.g.*, $SiCl_3Br$, are known.

Silicon fluoride, SiF_4.—The amorphous and crystalline varieties of silicon ignite spontaneously in fluorine, forming gaseous **silicon fluoride,** SiF_4. Pure silicon fluoride is obtained by heating barium fluosilicate: $BaSiF_6 = BaF_2 + SiF_4$. The gas is more conveniently prepared by the action of hydrofluoric acid on silica (Scheele, 1771): $SiO_2 + 4HF = SiF_4 + 2H_2O$. Since it is decomposed by water (see below), some dehydrating agent is added. Usually a mixture of powdered fluorspar and white sand in equal proportions is heated in a glass flask with three times its weight of concentrated sulphuric acid: $2CaF_2 + 2H_2SO_4 + SiO_2 = 2CaSO_4 + SiF_4 + 2H_2O$. The colourless gas, which fumes strongly in moist air, is collected over mercury. To free it from hydrogen fluoride, it may be passed over sodium fluoride. Silicates, such as glass, are also decomposed by hydrofluoric acid, with evolution of silicon fluoride.

Silicon fluoride is a colourless, incombustible, strongly fuming gas, with a normal density of 4·693 gm./lit. It solidifies, without previous liquefaction, at $-97°$ under atmospheric pressure. The solid melts at $-77°$ under 2 atm. pressure, and the liquid boils at $-65°$ under 1810 mm. pressure. Ammonia solution decomposes it with separation of gelatinous silica: $SiF_4 + 4NH_4OH = Si(OH)_4 + 4NH_4F$.

When silicon fluoride is passed over heated silicon, a **subfluoride** (? Si_2F_6) is said to be formed as a white powder, which reduces potassium permanganate solution.

Silicon fluoride forms with ammonia gas a white crystalline compound, $SiF_4,2NH_3$.

The compound $SiHF_3$, **silico-fluoroform,** analogous to silicon chloroform, is obtained by the action of stannic fluoride, or titanium tetrafluoride, on the latter, and is a combustible gas, b.-pt. $-80{\cdot}2°$, m.-pt. $-110°$, which decomposes on heating: $4SiHF_3 = 3SiF_4 + 2H_2 + Si$, and on contact with water:

$$2SiHF_3 + 4H_2O = Si(OH)_4 + H_2SiF_6 + 2H_2.$$

Hydrofluosilicic, or silicofluoric, acid, H_2SiF_6.—The reaction between silicon fluoride and water, discovered by Scheele in 1771, but only completely explained by Berzelius in 1823, leads to the formation of gelatinous silica and a new soluble acid, H_2SiF_6 (or $SiF_4 \cdot 2HF$), called **hydrofluosilicic acid,** or **silicofluoric acid**: $3SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6$. If the gelatinous liquid so formed is treated with hydrofluoric acid until the silica is just dissolved, more hydrofluosilicic acid is formed, and the difficult process of filtration is avoided: $Si(OH)_4 + 6HF = H_2SiF_6 + 4H_2O$.

EXPT. 313.—Heat a mixture of 50 gm. of powdered fluorspar, 50 gm. of fine white sand, and 100 c.c. of concentrated sulphuric acid in a stout glass flask (thin glass is soon perforated) on a sand-bath, and pass the silicon fluoride (fuming in air) into water in a cylinder, the gas delivery tube dipping under an inch of mercury at the bottom to prevent the tube becoming choked by the gelatinous silica (Fig. 369). The latter is deposited in strings of small sacs, each enclosing a bubble of gas; these should be broken down occasionally by stirring with a glass rod. The liquid is then filtered through linen, and the silica, when washed, dried, and heated, is very pure (sp. gr. 2·2).

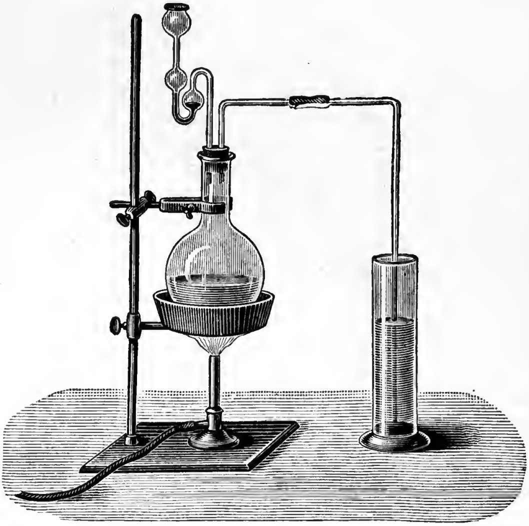


FIG. 369.—Preparation of Hydrofluosilicic Acid.

Priestley, in describing this experiment ("Observations on Air"), remarks: "I have met with few persons who are soon weary of looking at it, and some could sit by it almost a whole hour and be agreeably amused all the time."

A concentrated solution of hydrofluosilicic acid fumes in the air. If silicon fluoride is passed into concentrated hydrofluoric acid cooled in ice, crystals of $H_2SiF_6,2H_2O$, m.-pt. 19°, separate. When solutions of the acid are titrated with alkali the following reactions occur:

1. $H_2SiF_6 + 2NaOH = Na_2SiF_6$ (pp.) $+ 2H_2O$.
2. $Na_2SiF_6 + 4NaOH = 6NaF + Si(OH)_4$ (pp.).

The end-point is therefore reached, with phenolphthalein, when *six* molecules of base have been added per molecule of acid.

Pure hydrofluosilicic acid does not corrode glass, but on evaporation it decomposes: $H_2SiF_6 \rightleftharpoons SiF_4 + 2HF$, and the hydrofluoric acid set free corrodes a flask or porcelain basin. With steam at high temperatures, crystals of silica are formed.

Hydrofluosilicic acid is obtained as a by-product in the manufacture of superphosphate by treating minerals containing *apatite* with sulphuric acid (p. 849).

Salts of hydrofluoric acid are called **silicofluorides,** or **fluosilicates;** they are prepared by adding the requisite amount of base to the acid, or by the action of gaseous silicon fluoride on the solid fluorides: $SiF_4 + 2NaF = Na_2SiF_6$. The following salts are difficultly soluble, and are precipitated when hydrofluosilicic acid is added to solutions of salts of the metals: Li_2SiF_6, K_2SiF_6, Na_2SiF_6, $BaSiF_6$, $CaSiF_6$, $YSiF_6$. The salts K_2SiF_6 and Na_2SiF_6 (which may be used in the preparation of silicon by heating them with alkali-metals: $K_2SiF_6 + 4K = 6KF + Si$) are formed as nearly transparent gelatinous precipitates; $BaSiF_6$ forms a white crystalline precipitate; strontium salts are not precipitated.

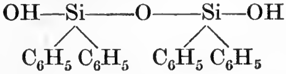
Silicon carbide, or carborundum, SiC.—If a mixture of sand and crushed coke in the proportions 5 : 3, with a little salt and sawdust, is heated electrically to 1550–2200° by a carbon rod passing through the mass (*cf.* graphite), **carborundum,** or **silicon carbide,** SiC, is formed: $SiO_2 + 3C = SiC + 2CO$. This compound, discovered by Acheson in 1891, is manufactured in large quantities at Niagara for use as an abrasive instead of emery, since it is nearly as hard as the diamond. The technical product is a black, coarsely-crystallised mass exhibiting a play of iridescent colours. It is very difficultly fusible, and may be used in furnace-linings. Carborundum resists all reagents except fused caustic soda exposed to air, which slowly acts upon it: $SiC + 4NaOH + 2O_2 = Na_2CO_3 + Na_2SiO_3 + 2H_2O$. Pure carborundum forms transparent, colourless or green, six-sided plates, sp. gr. 3·1, and is obtained by fusing silicon with carbon in the electric furnace.

The carborundum in the electric furnace is found to be surrounded by a layer of **siloxicon,** which is said to be a definite compound, Si_2OC_2, mixed with a little **silicon monoxide,** SiO, but may be a solid solution of silica in silicon carbide. It is used as a refractory. A fibrous variety, called **fibrox,** is used as a heat insulator instead of asbestos.

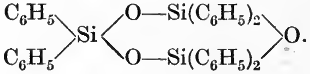
Silicon borides, SiB_3 and SiB_6, which are very hard, are formed in the electric furnace. **Silicon nitrides,** SiN_2, Si_2N_3, and Si_3N_4, are produced when nitrogen is passed over heated silicon. **Silicon disulphide,** SiS_2, is formed in white silky needles by heating silicon in sulphur vapour; it is instantly decomposed by water into sulphuretted hydrogen and gelatinous silica. It is also formed by passing the vapour of carbon disulphide over a strongly-heated mixture of silica and carbon: $SiO_2 + CS_2 + C = SiS_2 + 2CO$.

Organic compounds of silicon.—A few compounds have been prepared by Kipping which contain chains or rings of alternate silicon and oxygen atoms, and are similar to organic carbon compounds. The maximum number of silicon atoms yet obtained in such compounds, however, is 4, whereas hydrocarbons containing 60 carbon atoms in the chain are known. Examples of Kipping's compounds are:

1.



2.



EXERCISES ON CHAPTER XXXV

1. How are boric acid and borax obtained? Starting with borax, how would you prepare: (*a*) boric acid, (*b*) boron chloride, (*c*) boron hydride?

2. Describe briefly the properties of boric acid. What happens when a solution of borax is added to: (*a*) concentrated hydrochloric acid, (*b*) a solution of calcium chloride?

3. How is boric acid recognised in analysis? How and why is it removed from solutions containing it which are to be tested for metals?

4. Describe briefly the preparation and properties of the hydrides of boron.

5. How is boron prepared? What are its properties?

6. How are boron chloride and boron fluoride prepared? What is the action of water on these substances?

7. Borax, on heating, loses 47·13 per cent. of its weight of water of crystallisation. Assuming the formula of the salt to be $Na_2B_4O_7,10H_2O$, and the atomic weight of sodium and oxygen to be 22·83 and 15·88, respectively, find the atomic weight of boron.

8. How may pure silica be obtained from a mineral silicate? From silica, how would you prepare: (*a*) silicon, (*b*) silicon chloride, (*c*) hydrofluosilicic acid? Describe the properties of these substances.

9. Describe briefly the halogen compounds of boron and silicon. In what respects do these two elements resemble, and differ from, carbon?

10. Describe the technical preparation of silicon and silicon carbide. For what purpose are these substances used?

11. In what forms does silica exist? How are the natural silicates classified?

12. How is colloidal silica made? What are the general properties of colloids, and in what respects do they differ from crystalloids?

13. Describe briefly the preparation and properties of the hydrogen compounds of silicon. How is silicon chloroform prepared, and what is the action of alcohol upon it?

CHAPTER XXXVI

SPECTRUM ANALYSIS

The spectrum.—If a solid or liquid is heated to a sufficiently high temperature it becomes luminous. At very high temperatures, the light emitted is white (*e.g.*, the limelight, p. 189). Such white light, or sunlight, when passed through a glass prism, is broken up into a series of coloured rays, called a **spectrum.** In passing through the prism the white light is sorted out into rays of different colours, which are bent or refracted by the prism to different extents. The red rays are the least refracted, whilst the violet rays suffer the largest deviation. The resulting **spectrum,** which may be received on a white screen (Fig. 370), shows the colours in the following order, beginning with the least refrangible: red, orange, yellow, green, blue, indigo, and violet. This is known as a **continuous spectrum,** since the colours shade into one another without any gaps. At the red end of the spectrum, but beyond the visible part, there are also rays which may be detected by their heating effect on a thermometer with a blackened bulb. These are the **infra-red rays.** Beyond the violet there are also invisible rays, which may be detected by causing the fluorescence (p. 8) of quinine salts and some other substances. These are the **ultra-violet rays.**

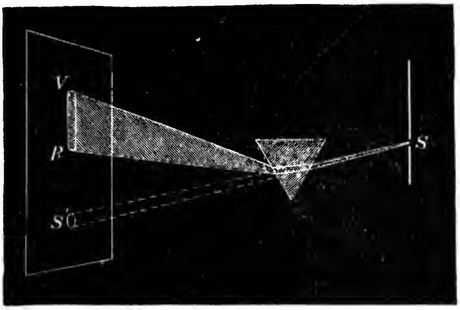


FIG. 370.—The Spectrum.

Each coloured ray and each kind of radiation beyond the visible spectrum at both ends is characterised by a definite **wave-length.** Light and allied invisible radiations consist of transverse vibrations in the hypothetical ether, and the waves resulting from the periodic vibrations differ in length according to the quality of the radiation. The infra-red waves are the longest and the ultra-violet waves the shortest in the spectrum. The average wave-length in the visible spectrum is about 5×10^{-5} cm. Wireless waves are very long waves in the ether; *X*-rays and the γ-rays from radium are very short waves. Wave-lengths of radiation are usually measured in **tenth metres,** *i.e.*, 10^{-10} m., or **Ångström units** (Å.U.), as they are sometimes called. The μ and $\mu\mu$ units (p. 8) may also be used.

The following table gives the wave-lengths of all parts of the spectrum so far investigated. The numbers range from 0·07 to 10^{14} Å.U.; the visible spectrum extends only over the very restricted range of 4000 to 7000 Å.U.

WAVE-LENGTHS IN ÅNGSTRÖM UNITS.

Wireless waves	10^{14} to 4×10^7	Blue	4550 to 4920
Infra-red	$3{\cdot}1 \times 10^6$ to 7230	Indigo	4240 to 4550
Red	6470 to 7230	Violet	3970 to 4240
Orange... ...	5850 to 6470	Ultra-violet ...	600 to 3970
Yellow ...	5750 to 5850	*X*- and γ-rays	8·4 to 0·07
Green	4920 to 5750		

The gap between the ultra-violet and *X*-rays has been partially bridged by short radiations recently measured in the hydrogen spectrum (Lyman).

Varieties of spectra.—If the light from a piece of platinum wire heated by an electric current is passed through a prism, it is found that at lower temperatures the red end of the spectrum alone appears, corresponding with the red light emitted by the body. With increasing temperature the visible spectrum extends gradually towards the violet, and when a dazzling white light is emitted, a **continuous spectrum** is obtained.

If small quantities of various salts, such as sodium, potassium, lithium, thallium, and strontium chlorides, are heated on platinum wires in a non-luminous Bunsen flame, it will be seen that the different salts impart characteristic colours to the flame:

sodium salts: yellow
potassium salts: purple
lithium salts: crimson
thallium salts: green
strontium chloride: red
calcium chloride: orange-red

If the light emitted by each of these coloured flames is passed through a prism, the spectra produced are not continuous, but consist of one or more bright **lines,** each corresponding with a definite wave-length. A spectrum of this kind is known as a **line spectrum,** and incandescent gases and vapours, produced by the volatilisation of salts in the flame, differ from solids or liquids in emitting line spectra instead of continuous spectra. No two lines given by different elements occupy exactly the same position in the spectrum, although they may be very close together, so that the spectrum of every element is characteristic, and may serve for the identification of the element. This is the principle of **spectrum analysis,** introduced into chemistry by Bunsen and Kirchhoff in 1860. A chart of spectra, with the wave-lengths of the principal lines, will be found on the inside of the front cover.

The visible spectra of salts usually correspond with those of the metals contained in them. The spectrum of sodium chloride, for example, is identical with the spectrum of metallic sodium. This shows that the vapours of the salts at the high temperature of the flame are dissociated, or broken down, into their elements. In some cases a compound exhibits a characteristic spectrum, superposed on that of the metal. This is the case with calcium chloride, which first gives a spectrum of the chloride, and later a spectrum corresponding with calcium oxide.

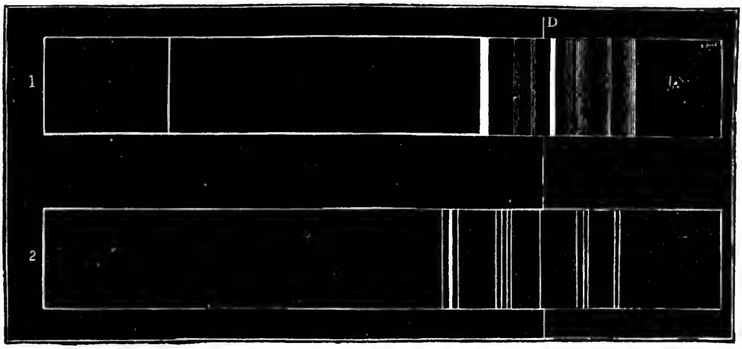


FIG. 371.—Band Spectra.

The spectra of compounds differ from those of elements in appearance. Instead of sharp lines, the spectrum consists of broad luminous **bands,** with a fluted appearance (Fig. 371), sharply defined at one edge, called the *head* of the band, and shading off at the other edge. A spectroscope of high resolving power, *i.e.*, one which separates the different lines as widely as possible, shows that the bands consist of large numbers of fine lines, very close together at the head of the band, but more and more widely separated towards the blurred edge of the band. Fig. 371 shows the band spectrum of calcium chloride, with the line spectrum of calcium below.

The spectroscope.—A convenient instrument for examining spectra is the **spectroscope,** invented by Bunsen and Kirchhoff. The most useful form for chemical purposes, which is that originally used by these investigators, is shown in Fig. 372. It consists of a prism, *a*, of flint glass, supported on an iron stand, and a brass tube, *b*, called a collimator, which is fitted at the end furthest from the prism with an adjustable slit, *d*, shown in Fig. 373. In this way a narrow line of light from the Bunsen flame, *e*, in which the substance is heated, is focussed on the prism, the rays being made parallel by a lens in the collimator. The light passing through the prism is received by the telescope, *f*, which may be moved round so as to embrace any part of the spectrum, and contains a lens which gives a magnified view of the spectrum in the eye-piece. In order to fix the position of any particular line, the image of a glass scale, fixed in the third tube, *g*, and illuminated by a candle or luminous gas flame, is thrown by reflection from the face of the prism into the telescope, and appears above the spectrum. The position of the line is then read off by comparison with this scale, and may be compared with the positions of lines given by standard elements.

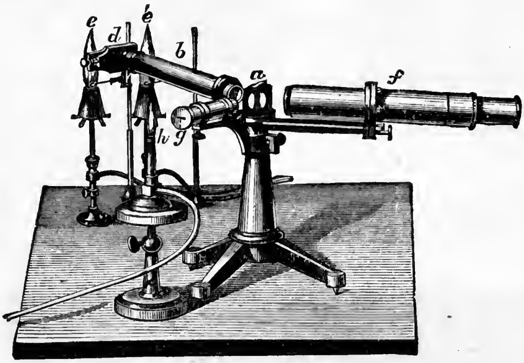


FIG. 372.—Simple Spectroscope.

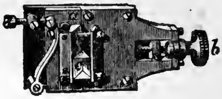


FIG. 373.—Adjustable Slit of Spectroscope.

A convenient form of spectroscope for qualitative work is the **direct vision** instrument, shown in section in Fig. 374. In this the spectrum produced by the flint glass prisms, *F*, is kept in a horizontal direction by the prisms of crown glass, *C*, so that a virtual image of the slit is seen by the eye at the lens, *E*. This instrument is very small and handy, and can be carried in the pocket.

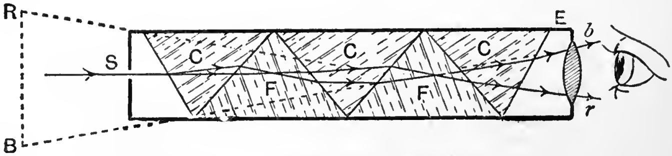


FIG. 374.—Direct-vision Spectroscope.

Production of spectra.—The spectra of **gases** may be observed in the light emitted by the gas at low pressure (1–2 mm.) when subjected to the electrical discharge from a coil in a Geissler tube (Fig. 105). Volatile salts may be heated on platinum wire, moistened with hydrochloric acid, in a Bunsen flame; or a small fused bead of the salt (usually the chloride) heated on the wire. The spectra of liquids may be obtained by taking electric sparks near the surface between platinum wires, as shown in Fig. 375, one or two Leyden jars being put in parallel with the coil; whilst the spectra of difficultly volatile substances are obtained by heating a small quantity of the material in a little hollow in the lower carbon rod of the electric arc. The spectra of some metals (*e.g.*, iron) may be obtained by striking an arc, or passing powerful sparks, between rods of the substance.

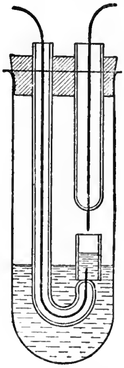


FIG. 375.—Apparatus for Producing Spark Spectra.

If the invisible parts of the spectrum are to be examined, the prisms and lenses must be of rock-salt for the infra-red, or quartz for the ultra-violet, since these rays are absorbed by glass. The infra-red spectrum is examined by means of its heating effect when the radiation is absorbed by a blackened strip of platinum called a **bolometer,** the electrical resistance of which increases with the temperature. A similar but shielded strip is placed in the opposite arm of a Wheatstone bridge. Langley's bolometer, used in mapping the solar infra-red spectrum, indicated a rise of temperature of 10^{-8} degrees. The ultra-violet spectrum is rendered visible by a fluorescent screen covered with barium platinocyanide, but is most conveniently recorded by its action on a photographic plate. In this case, a camera is attached to the spectroscope, the latter being equipped with quartz prisms. Since the extreme ultra-violet rays are absorbed by air, or the gelatin of a photographic plate, this portion of the spectrum ("Schumann rays") must be investigated with the whole apparatus in an evacuated chamber, and a silver bromide film prepared without gelatin.

Variation of spectra.—Bunsen and Kirchhoff considered that the spectrum of an element was always exactly the same, each line having an invariable wave-length. Plücker and Hittorf in 1865, however, found that nitrogen in a vacuum tube could emit two different spectra, one a line spectrum, and the other a band spectrum. Both spectra may be emitted simultaneously, and the phenomenon has been observed with many other substances. Phosphorus emits eight different kinds of spectra. Variations of pressure in gases lead to broadening and even to slight displacements of spectrum lines, and the invariable position of spectrum lines under all conditions is no longer recognised. It has been found, for instance, that slight differences exist in the positions of lines in the iron spectrum given by the sun (see below) and by the iron-arc, respectively. The admixture of small quantities of gases may also appreciably alter the relative intensities (not the positions) of the lines in the spectrum of another gas.

In the case of certain elements, the spectroscope is capable of revealing the presence of very minute quantities of the substance—far below the possibility of detection by chemical analysis. A quantity of $\frac{1}{3000000}$ mgm. of sodium may be detected, and all materials show the spectrum of this element. In other cases the spectroscope may be much less sensitive, and sometimes the spectrum of one substance may be practically extinguished by traces of other substances.

The solar spectrum.—In 1802 Wollaston, examining sunlight passing through a slit by means of a prism placed before the eye, noticed that the spectrum was crossed by a large number of fine **black lines**. These dark lines in the solar spectrum were carefully mapped by Fraunhofer in 1814, who found that they always occurred in the same position in the spectrum. The lines are called **Fraunhofer's lines**, and the most important are designated by alphabetical letters. Fraunhofer suggested that they were caused by the **absorption** of the particular parts of the spectrum by the passage of the light through the atmosphere of incandescent gases surrounding the sun. The explanation of the cause of the dark lines was, however, first clearly stated by Kirchhoff in 1860. He brought near the slit of the spectroscope, through which he was examining the solar spectrum, a flame charged with sodium vapour. The two very nearly coincident dark lines in the solar spectrum, called D by Fraunhofer, at once changed into the two bright yellow lines of the sodium spectrum. The latter were therefore coincident with the dark D-lines of the solar spectrum. Kirchhoff then exchanged the sunlight for limelight, which gives a continuous spectrum having no dark lines. On placing a sodium flame between the source of this light and the slit of the spectroscope, the two dark D-lines at once appeared.

Kirchhoff observed that this result is easily explained on the supposition that the sodium flame absorbs the same kind of rays as it emits, whilst it is perfectly transparent to other rays. If the intensity of the light passing through the flame is greater than that of the same kind emitted by the flame, the absorption in the latter will cause such a weakening of intensity in that part of the spectrum that the lines will appear dark in contrast with the rest of the spectrum.

If we imagine a piano played in the middle of a room which is otherwise filled with wires stretched so as to emit one particular note only, say the c′ of 256 vibrations per second, then a person outside the room would hear all the notes except this one. These particular vibrations are taken up by the stretched wires, which are in resonance with them, and cause the latter to vibrate. The sound emitted by the wires is, however, too feeble to be heard among the other louder notes, which have not suffered absorption.

If the light emitted by a burning piece of sodium is examined by a spectroscope, the two D-lines will be seen reversed, as dark lines, on the background of a continuous spectrum. The solid particles of incandescent sodium oxide produced in the flame emit a continuous spectrum, but the sodium vapour absorbs most of the yellow rays from this light.

EXPT. 314.—Pass a stream of hydrogen through a Woulfe's bottle in which hydrogen is produced from zinc and dilute hydrochloric acid containing common salt. The gas is burnt as a large flame, coloured yellow by sodium from the spray, at a burner *A* (Fig. 376). A small Bunsen burner *B*, with a head of sodium chloride, is placed in front of the large flame. The outer edge of the small flame appears dark against the bright yellow background.

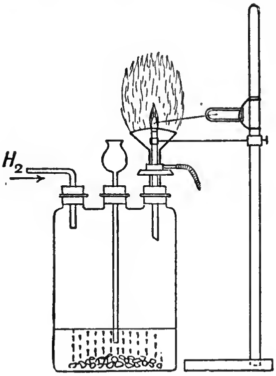


FIG. 376.—Reversal of Sodium Line in Spectrum.

The presence of sodium vapour in the atmosphere of the sun may therefore be inferred from the *dark* lines in the spectrum. The *bright* parts of the spectrum teach us nothing as to the elements present in the sun, because they are merely parts of the continuous spectrum emitted by *any* solid body raised to incandescence. It has been shown that a sufficiently thick layer of incandescent gas will also emit a continuous spectrum, and this probably corresponds with the constitution of the sun. It is the *dark* lines of the spectrum, corresponding with absorption in the solar atmosphere, which indicate the presence of corresponding elements in the latter. By examining these lines the composition of the sun, given on p. 32, has been discovered.

Certain stars and nebulæ, however, show *bright* lines on a dark ground. These correspond with elements present in the masses of incandescent gas or vapour.

The spectroscope, therefore, opened the way to the chemical examination of bodies in space; the rays of light coming from the most distant stars reveal the chemical composition of the luminous matter with as much certainty as if the millions of miles of intervening space had been annihilated, and a sample of the star placed on the bench in the laboratory.

Absorption spectra.—If white light is transmitted through a transparent coloured body, such as ruby glass, or a solution of indigo, the emergent light, if examined by the spectroscope, is found to have lost certain portions of the spectrum. These constituents have been **absorbed** by the body, and the remaining part of the spectrum corresponds with the colour of the body. A solution of copper sulphate removes all the spectrum except the blue end; a solution of potassium dichromate removes all except the red end. In other cases dark bands, corresponding with absorption, cross the spectra at various parts.

The absorption spectrum differs in most cases from the emission spectrum of the same substance. The dark absorption lines of chlorine gas are not even analogous to the bright lines in the emission spectrum. In the case of iodine, however, the two sets of lines correspond. The absorption spectra of solutions are nearly always made up additively of one or two sets of bands, corresponding with one or both of the two ions, respectively. All permanganates, for example, show the same bands, characteristic of the ion MnO_4'. With concentrated solutions the absorption due to the undissociated molecules makes its appearance, and in the case of the nitrates, each salt shows a characteristic ultra-violet absorption spectrum, differing according to the metal present.

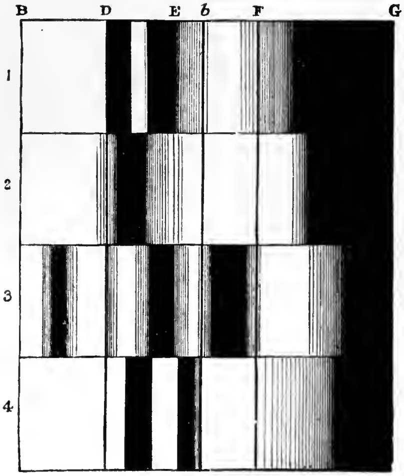


FIG. 377.—Absorption Spectra of Blood.

The absorption spectra of blood are shown in Fig. 377. No. 1 shows two dark bands, D and E, due to oxyhæmoglobin, given by oxidised blood. No. 2 shows the absorption spectrum of de-oxidised blood, in which there is only one dark band, due to hæmoglobin. By the action of acids on blood, the hæmoglobin is converted into hæmatin, the oxidised and de-oxidised forms of which give the spectra Nos. 3 and 4. Carbon monoxide and hydrocyanic acid form compounds with hæmoglobin, giving characteristic absorption spectra.

Determination of wave-lengths by the spectroscope.—The position of any spectrum line is determined by the scale in the instrument, the position marked 50 being adjusted on the double sodium line. The scale-readings, however, vary with the particular type of glass used in making the prism, *i.e.*, with the dispersion of the prism, and these numbers are therefore arbitrary. The real characteristic of a spectrum line is the **wave-length** of the light producing the line, and in the identification of substances it is necessary to find the wave-lengths of the lines in its spectrum, and compare these with the tables of wave-lengths, or with the spectrum chart on p. 1041. The wave-length is obtained by interpolation on a **wave-length curve.** The positions of the lines on the arbitrary scale are plotted as abscissæ, and the wave-lengths of standard lines, the position of which is found also on the arbitrary scale of the spectroscope, are plotted as ordinates. If the ordinates are joined in a smooth curve, the ordinates of the points where verticals from the scale readings cut the curve give the required wave-lengths. The standard lines shown in the chart may be used. The colour of a line may be inferred from its wave-length by means of the list on p. 756.

EXERCISES ON CHAPTER XXXVI

1. Describe the chief characteristics of the spectra of (*a*) an incandescent solid, (*b*) an incandescent gas. What use is made of these in chemistry ?

2. What are absorption spectra ? What regularities have been noticed in the absorption spectra of salts, and how are they explained ?

3. What is known of the composition of the sun, and other stars ? How has this knowledge been obtained ?

CHAPTER XXXVII

METALS AND ALLOYS

Metals.—The metals **gold, silver, copper, iron, tin,** and **lead** were known to the ancients: they are mentioned in the Old Testament, and by early Greek authors. **Mercury** is mentioned by Aristotle (B.C. 384–322). **Zinc** is referred to by Paracelsus (1539), and **bismuth** by Agricola (*c.* 1530). **Antimony** and its compounds are carefully described by the supposed Basil Valentine. The remaining metals have all been discovered since the seventeenth century. Mercury was definitely included among the metals only after its solidification by cold, which was noticed in a severe Russian winter by Braune, in 1759.

The metals occur chiefly in veins traversing granitic, or limestone, rocks; more rarely in detached nodules in alluvial strata. Only a few, viz., gold, silver, copper, mercury, and the platinum metals, occur in the metallic, or **native,** state; the rest occur as **ores,** mostly oxides and sulphides, or carbonates and sulphates.

The **general properties of metals** have been referred to (p. 450). The first distinct definition of a metal was, apparently, given by the Latin Geber (p. 29): "A metal is a miscible and fusible body, which is extensible in all directions under the hammer." This excludes the brittle metals, which were classed as **semi-metals.** Fourcroy (1789) pointed out that such distinctions are too arbitrary to be of use: between the perfectly malleable gold and the brittle antimony there are insensible gradations. The exact characteristics which separate metals from non-metals cannot, in fact, be described, and an element like tellurium may be regarded either as a metal (from its physical properties), or as a non-metal (from its chemical analogies to sulphur).

The alchemists regarded metals as compounds of mercury and sulphur (p. 29), and this idea lasted until the end of the seventeenth century. Thus, Wilson ("Compleat Course of Chymistry," London, 1721) speaks of gold as: "by Nature generated of a most pure fixed *Mercury*, and a small quantity of clean fix'd Sulphur, of most pure Redness, which tingeth the *Mercury*." The sulphur and mercury of metals were not, however, regarded as the ordinary materials, but were occult principles.

Thomas Norton (1477) says, in connection with the alchemical principles: " Our gold and silver are not those you can hold in the hand."

Stahl, and the phlogistonists, considered the metals to be compounds of phlogiston with the calx of the metal (*i.e.*, its oxide). Lead is converted by heating in the air into a dross, or *calx*, and it was supposed that phlogiston escaped. By heating the calx of lead with charcoal, a substance rich in phlogiston, the metal was revived: metal = calx + phlogiston.

Lavoisier (1787) recognised the elementary character of the metals, and gave a list of the seventeen metals then known, in his tables of the elements.

The existence of **allotropic forms** of some metals (*e.g.*, gold) was discovered by Matthiessen; more recent investigations have shown that several metals can exist in allotropic forms. Some of these are well-defined: ordinary tin forms a grey modification on cooling, and three kinds of iron are recognised. In other cases the existence of allotropy is only inferred from peculiarities in the expansion of the metal by heat, and the different forms have not been isolated.

Alloys.—If two or more metals are fused together they usually, but not always (*e.g.*, zinc and lead, p. 821), form a homogeneous liquid, and the intimate association of the metals which is formed on solidification is called an **alloy.** The name alloy, which was used in this sense by Chaucer, is derived from the Latin *alligare*, " to bind to." Although the preparation of alloys by fusion is the method most commonly used, the strong compression of finely-powdered metals, the simultaneous electro-deposition of the metals from a mixed solution (*e.g.*, copper and zinc, in the form of brass, from a solution of the cyanides in potassium cyanide), and the reduction of one or more of the metals from compounds in the presence of the other metal (*e.g.*, aluminium from the oxide by carbon in the electric furnace in presence of copper to form aluminium bronze), are alternative processes leading to the formation of alloys. Alloys containing mercury are called **amalgams,** a word which may have been derived from Arabic.

The solid formed by the solidification of a fused mixture of metals may be either (*a*) homogeneous, or (*b*) heterogeneous.

The **homogeneous solid alloy** may be:

(i) *a solid solution*,
(ii) a *pure chemical compound*, or
(iii) a *solid solution of a compound in excess of one of the metals.*

Compounds of metals with non-metals may also be present in alloys; *e.g.*, hard steel, prepared by quenching, is a solid solution of iron carbide, Fe_3C, in a particular allotropic form of iron (**γ-iron**).

Allotropic forms of some metals, which differ from the ordinary form, may occur in the alloys.

An alloy of platinum and silver may dissolve completely in nitric acid, whilst platinum itself is insoluble; an alloy of 10 per cent. of gold with potassium, when thrown into water, leaves the gold as black powder, which forms a colloidal solution with water; this form is converted into ordinary yellow gold by heating to redness.

If the solid alloy is **heterogeneous,** the separate phases (p. 106) may consist of:

(i) *pure metals,*
(ii) one or more *pure compounds,* or
(iii) *solutions* of metals, or compounds, in metals.

Freezing-point curves of alloys.—The class to which an alloy belongs may be determined by an examination of the **freezing points** of fused mixtures of the constituents in various proportions. For simplicity we shall consider only two components, **X** and **Y,** forming a **binary alloy,** and shall suppose that this alloy either (*a*) is a heterogeneous mixture of the two pure components, or (*b*) consists of one or more chemical compounds, with or without an excess of one of the pure components. The consideration of solid solutions is more difficult, and is omitted.

We consider first the case in which no chemical compounds of the metals are present in the alloy. If the pure metal, **X,** say silver, is fused, and allowed to cool, it will begin to solidify (if supercooling is absent) at the freezing point. This may be represented on a diagram (Fig. 378) by the point *A*. In the diagram, the temperature of solidification is measured vertically, and the composition of the alloy is represented on the horizontal by dividing the latter into 100 parts, each representing one atomic proportion in 100 atomic proportions of total alloy. Thus, the end, *P*, of the line must correspond with 0 part of the second metal, **Y,** say lead, and the point *A* on the vertical line above *P* represents the melting point of pure silver (atoms of lead = 0; atoms of silver = 100). The point *Q* will then represent pure lead (atoms of lead = 100;

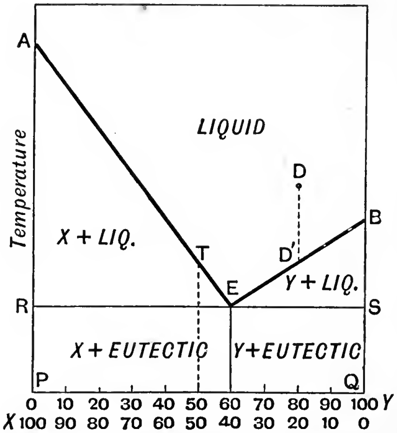


FIG. 378.—Freezing Point Curves of Binary Alloy Forming Eutectic.

atoms of silver = 0), and *B* is the melting point of pure lead. A point midway on the line *PQ* represents a mixture of equiatomic amounts of lead and silver (atoms of lead = 50; atoms of silver = 50). The proportions of lead in the alloys are represented on the upper scale, those of silver on the lower scale; the sum is always 100.

If a little lead is added to the silver, the fused alloy will begin to solidify at a temperature slightly lower than the melting point of pure silver, since a dissolved substance (in this case lead) lowers the freezing point of a solvent (in this case silver), provided the pure solvent separates on cooling (p. 104). This temperature will be represented by a point a little to the right of *A*. By adding successive amounts of lead, the freezing points become progressively lower, and they will lie on a curve such as *AE*. If the molecular depression of freezing point were constant, this would be a straight line, which has been drawn in Fig. 378 for simplicity; usually *AE* is not straight, since the laws of dilute solutions do not apply strictly. The depression of freezing point will continue as more lead is added, until at a certain point, E, both silver and lead begin to separate side by side. This is the **eutectic point** (p. 104), and is the lowest temperature at which solidification of the alloy can begin. A mixture containing the metals in the proportions corresponding with the eutectic mixture (60 : 40 in the diagram) will solidify completely at the eutectic temperature.

Exactly the same conditions apply to the addition of silver to lead. In this case the freezing points of various alloys lie on the curve *BE*, running down from the freezing point, *B*, of pure lead. The eutectic point, *E*, is again reached, when silver begins to separate along with the lead.

At all points above the region *AEB* in the diagram the alloy is entirely liquid; if a horizontal line, *RS*, is drawn through *E*, then at all temperatures included in *ARE* pure silver separates from fused alloys having compositions given by the lower line beneath *RE*. In the region *BSE* pure lead separates. At the eutectic temperature, represented by *RS*, lead and silver separate together. At temperatures below *RS* the whole is solid.

Now consider what occurs when a fused alloy represented by the point *D* is cooled. It remains liquid until the temperature has fallen to such a point that the curve *EB* is intersected at *D*. Since the curve *EB* corresponds with separation of lead, this metal will now begin to separate in the solid state. The still liquid part will become richer in silver (since pure lead has separated), and will freeze at a somewhat lower temperature. Both the composition and freezing point will now be represented by a point on the curve nearer *E*. As solidification proceeds, the temperature falls, until finally the eutectic point *E* is reached, when silver begins to separate along with the lead, and the whole mass then solidifies at the eutectic temperature.

If the solid alloy resulting from the above experiment is polished, etched with a suitable reagent, and examined under the microscope with light reflected from the metallic surface, we shall see crystals of lead, which separated along *D'E*, embedded in a matrix of eutectic alloy. The latter is always composed of small crystals. The large cubes in Fig. 379 represent the first constituent to separate from an alloy, embedded in a eutectic matrix.

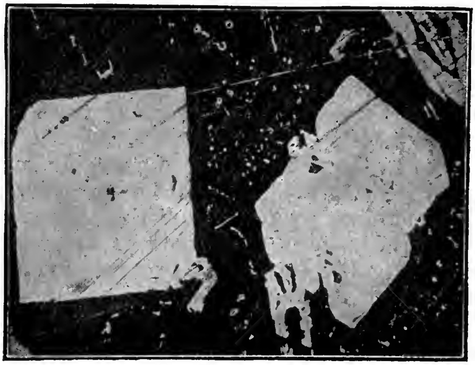


FIG. 379.—Microscopic Appearance of Solidified Alloy.

In the second place we will consider an alloy in which metallic compounds are formed, say tin and magnesium, which form Mg_2Sn. A hypothetical curve is shown in Fig. 380.

The compound of **X** and **Y**, say $\mathbf{XY_2}$, will have a definite melting point, represented by *C*. If pure **X** is added to the fused compound, or to a mixture of **X** and **Y** in the requisite proportions to form $\mathbf{XY_2}$, the freezing point is lowered along CE_1, since the compound now acts as a solvent for **X.** The solid separating along CE_1 is pure $\mathbf{XY_2}$. Finally, a eutectic point, E_1, is reached, at which $\mathbf{XY_2}$ and **X** separate together. If $\mathbf{XY_2}$, or pure **Y**, is added to pure **X**, the freezing point of the latter is depressed along AE_1, the solid separating being pure **X**, until E_1 is again reached, when **X** and $\mathbf{XY_2}$ separate. The solid alloy obtained on cooling a liquid mixture of composition *C* will be homogeneous $\mathbf{XY_2}$. An alloy formed by the complete solidification of a liquid of a composition enclosed within the verticals between *C* and E_1 will consist of

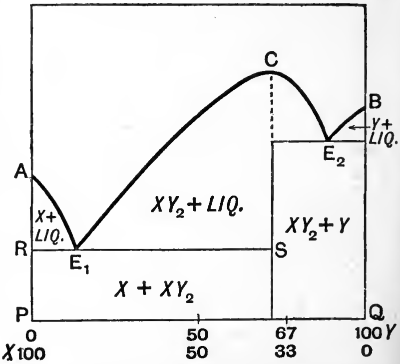


FIG. 380.—Freezing-point Curves of Binary Alloy Forming One Compound.

crystals of $\mathbf{XY_2}$ embedded in a matrix of a eutectic mixture of $\mathbf{XY_2}$ and **X**.

Exactly similar relations hold for the addition of an excess of **Y** to $\mathbf{XY_2}$, or $\mathbf{XY_2}$ to **Y**, when a second eutectic point E_2 will appear. Between E_2 and B pure **Y** separates; at E_2 the eutectic $\mathbf{XY_2} + \mathbf{Y}$ separates.

If we commence with pure **X** and add increasing amounts of **Y** until practically pure **Y** is obtained, the freezing points will make up the whole curve AE_1CE_2B, which has a maximum and two eutectics. A curve of this type is characteristic of the formation of one compound. If there are two compounds there will be two maxima, and so on. The rounded form of the maximum indicates that the compound is partially dissociated in the liquid state: $\mathbf{XY_2} \rightleftharpoons \mathbf{X} + 2\mathbf{Y}$. The microscopic appearance of a pure metal, or of an alloy which is a definite compound, is that of more or less large crystals which are practically in contact, since there is no eutectic matrix.

EXERCISES ON CHAPTER XXXVII

1. Give a brief account of the various opinions which have been held as to the nature of the metals. What are regarded as characteristic properties of metals ?
2. What are alloys ? How are they prepared, and into what groups may they be classified ?
3. Explain how it is possible, from the form of the freezing-point curves, to distinguish between alloys which are mechanical mixtures and those which contain chemical compounds.

CHAPTER XXXVIII

THE METALS OF THE ALKALIES

The alkali-metals.—Under the name **alkalies** are included the substances of formula ROH, potash, soda, ammonia, lithia, rubidia, and cæsia. The **metals of the alkalies** are therefore **potassium, sodium, lithium, rubidium,** and **cæsium.** The radical **ammonium,** NH_4, although it has not been isolated, behaves in its compounds as a univalent alkali-metal. It forms an amalgam with mercury, and thus exhibits metallic properties, so that ammonium compounds are usually considered with those of the alkali-metals.

The **properties of the alkali-metals** are shown in the table below.

	Lithium.	**Sodium.**	**Potassium.**	**Rubidium.**	**Cæsium.**
Density at 0°	0·59	0·9723	0·859	1·525	1·903
Melting point	180·1°	97·6°	62·04°	38·5°	25°
Boiling point	> 1400°	877°	758°	696°	670°
Atomic weight ($H = 1$)	6·89	22·82	38·79	84·77	131·76
Atomic volume	11·7	23·5	44·4	55·8	70·2
Colour of vapour	?	purple, green fluorescence	green	blue	?
Action on water...	slowly decomposes	rapidly decomposes, but does not burn	decomposes, and burns	decomposes, and burns	decomposes, and burns
Oxides ...	Li_2O	Na_2O, Na_2O_2	K_2O, K_2O_4	Rb_2O,Rb_2O_2, Rb_2O_4	Cs_2O,Cs_2O_2, Cs_2O_3,Cs_2O_4

The gradation in properties, with increasing atomic weight, is clearly seen. The metals of the alkalies are the most electro-positive elements known; they never produce acids, or complex anions, and displace all other metals from their salts. In the group itself, the electropositive character increases from lithium to cæsium, the latter being the most electropositive of the metals. The basicity of the hydroxides increases in the same manner.

The alkali-metals are **univalent**, forming salts of the type RX; although a few higher halogen compounds are known, these are very unstable:

$LiCl_4I,4H_2O$	KI_3	$RbBr_3$	$RbBr_2I$	RbI_7	$CsBr_3$	$CsCl_4I$
—	KI_7(?)	$RbClBr_2$	$RbCl_2I$	RbI_9	$CsBr_5$	CsI_9
—	KI_9(?)	$RbCl_2Br$	$RbClBrI$	—	CsI_3	—
—	$KICl_4$	RbI_3	$RbCl_4I$	—	CsI_5	—

The alkali-metals all combine directly with hydrogen, forming solid, non-metallic, **hydrides**, RH, decomposed by water: $RH + H_2O = ROH + H_2$.

The **vapour densities** of potassium and sodium have been determined approximately, and correspond with monatomic molecules: Na and K. In solution in tin, sodium also exists as single atoms.

Acids, bases, and salts.—Although typical representatives of these three important classes of chemical compounds have been studied in the preceding pages, and their general properties considered, no attempt has been made to give logical definitions of the groups. This is, in fact, a matter of some difficulty, since the properties of one can hardly be specified without reference to those of the other two members.

The ancients knew only one **acid**, viz., common *vinegar*, or crude **acetic acid**, produced by the oxidation of wine, which becomes **sour** on exposure to air (Greek *oxos*, vinegar; *oxus*, sour). They knew that vinegar effervesced with natural sodium carbonate (*nitrum*, Proverbs xxv, 20), and the solvent properties of acids figure in the story of Cleopatra and the pearl. Other acids (sulphuric, nitric, hydrochloric) were discovered by the alchemists; Scheele (1770–1786) isolated a number of **organic acids**, *i.e.*, acids containing carbon, hydrogen, and oxygen, of which acetic acid, $C_2H_4O_2$, is an example. These acids, such as **citric** ($C_6H_8O_7$), **tartaric** ($C_4H_6O_6$), and **malic** ($C_4H_6O_5$), impart a sour taste to unripe fruits, whilst the acidity of sour milk is due to **lactic acid** ($C_3H_6O_3$). Boyle (1663) recognised the following as the **properties of acids**:

(1) They possess a sour taste.

(2) They act as solvents, but with varying power on different bodies; the varying **strengths of acids** was recognised by Tachenius in 1666.

(3) They precipitate sulphur from a solution of liver of sulphur (polysulphides of potassium).

(4) They turn many blue vegetable colours (*e.g.*, litmus) red, the colour being restored by alkalies.

(5) They combine with alkalies, the characteristic properties of each substance disappearing, and a **neutral salt** being formed.

On the basis of these tests, Hoffmann (1723) and Black (1755) were able to show that carbonic acid occurring in mineral waters, is a true acid, though a weak one.

(6) Cavendish (1766) showed that hydrogen is evolved by the action of acids (except nitric) or zinc, iron, and tin.

Examples of **alkaline substances**, wood ashes, and *natron* (native sodium carbonate) were known to the ancients. The alchemists of the thirteenth century were acquainted with ammonium carbonate in the form of *spirit of hartshorn*, prepared by the destructive distillation of horn and bones, or the putrefaction of urine (*cf.* p. 801). Later on, it was found that the salt obtained by the lixiviation of the ashes of plants growing on the sea littoral had the same properties as natron, whilst seaweeds contained the same alkali as wood ashes. The Iatrochemists first described the general properties of alkalies. These properties were found to be enhanced by boiling with milk of lime, and the names **mild alkali** and **caustic alkali** were introduced for the alkali before, and after, this treatment, respectively.

As **general properties of alkalies,** the following were recognised:

(1) Their solutions feel soapy when rubbed between the fingers. (This is probably due to corrosion of the skin, since it is felt with concentrated sulphuric acid; acids when diluted usually feel very harsh when so treated.)

(2) They restore the blue colour of dyes reddened by acids (*e.g.*, red cabbage, litmus), and turn the extract of violets green.

(3) They neutralise acids to form salts.

(4) The "mild" varieties effervesce with acids, giving off "fixed air" (CO_2).

The difference between **potash**, from wood ashes, and **soda**, from *natron* or the ashes of marine plants, was established by Duhamel in 1737. Margraaf (1757) differentiated between potash and soda as follows:

	Potash.	**Soda.**
1. Heat on platinum wire in alcohol flame.	Colours the flame violet.	Colours the flame yellow.
2. Add platinic chloride to solution in hydrochloric acid.	Gives a yellow crystalline precipitate.	Gives no precipitate.

Scheele found that tartaric acid gives a white precipitate of cream of tartar with concentrated solutions of potassium salts, but no precipitate with sodium salts. The latter are precipitated by a solution of potassium pyroantimoniate (p. 936).

Black's researches on the alkalies.—The chemical nature of the alkalies was largely elucidated by the classical researches of Joseph Black (*b.* 1728—*d.* 1799), ("Dissertation on Magnesia," 1754). At that time three alkalies, and a mild and caustic form of each, were known :

(1) **Mild vegetable alkali** (potassium carbonate, K_2CO_3), obtained by the lixiviation of plant ashes. On boiling with lime, this gave the **caustic vegetable alkali** (potassium hydroxide, KOH).

(2) **Mild marine alkali** (sodium carbonate, Na_2CO_3), obtained in Normandy and Spain by the lixiviation of ashes of plants growing on the sea-shore (deep-sea weeds contain the vegetable alkali). With lime this gave the **caustic marine alkali** (sodium hydroxide, NaOH).

(3) **Mild volatile alkali** (ammonium carbonate, $(NH_4)_2CO_3$), obtained by the destructive distillation of bones, from fermented urine, or from the *sal-ammoniac* of Egypt. This gave a **caustic volatile alkali** (ammonium hydroxide, NH_4OH) with lime, as was recognised by Kunckel ("Laboratorium chymicum," published in 1716, fourteen years after his death).

According to the phlogistic theory then in vogue, limestone on burning absorbs **phlogiston**, or the "principle of causticity," from the fire, which imparts its properties to the quicklime :

$$\text{Limestone} + \phi = \text{quick (or caustic) lime.}$$

The process of converting a mild into a caustic alkali by boiling with quicklime was similarly regarded as transference of phlogiston :

$$\text{Mild alkali} + \phi = \text{caustic alkali.}$$

On boiling mild alkali with quicklime, the phlogiston was transferred from the quicklime to the alkali, rendering the latter caustic, whilst the lime was converted into limestone :

$$\underset{\substack{\text{or}\\ \text{Quicklime}}}{(\text{Limestone} + \phi)} + \text{Mild alkali} = \text{Limestone} + \underset{\substack{\text{or}\\ \text{Caustic alkali}}}{(\text{Mild alkali} + \phi)}$$

Black (who worked chiefly with magnesia, the mild form of which is easily decomposed by heat) succeeded in overturning this aspect of the theory of phlogiston. He found that when limestone is heated there is a loss of weight, and **fixed air** (CO_2) is disengaged. If the residual quicklime is dissolved in water, and boiled with mild alkali, a weight of limestone exactly equal to that taken for calcination in the first experiment is obtained ; it had therefore been exactly reproduced by taking fixed air from the mild alkali, leaving the latter caustic :

(1) Limestone = Quicklime + Fixed air (experimentally proved).
(2) Caustic alkali + Fixed air = Mild alkali (assumed).
(3) Quicklime + $\underbrace{\text{(Caustic alkali + Fixed air)}}_{\text{Mild alkali}}$ = $\underbrace{\text{(Quicklime + Fixed air)}}_{\text{Limestone.}}$ + Caustic alkali ;

(agreeing with assumption (2), and offering a simple explanation of causticising

In modern notation, these reactions are represented as follows :

$$\begin{aligned}
&(1)\ CaCO_3 &&= CaO + CO_2.\\
&(2)\ 2KOH + CO_2 &&= K_2CO_3 + H_2O.\\
&(3)\ CaO + H_2O + K_2CO_3 &&= CaCO_3 + 2KOH.
\end{aligned}$$

The assumption made in statement (2) was proved as follows. The same fixed air was obtained by the action of an acid on mild alkali as by the action of an acid on limestone, and the solution of limestone in an acid gave the original weight of limestone when precipitated by a mild alkali :

$$\begin{aligned}
CaCO_3 + 2HCl &= CaCl_2 + CO_2 + H_2O.\\
K_2CO_3 + 2HCl &= 2KCl + CO_2 + H_2O.\\
CaCl_2 + K_2CO_3 &= CaCO_3 + 2KCl.
\end{aligned}$$

Statement (3) then followed as a logical consequence of (1) and (2).

Black's results were disputed by F. Meyer (1764), whose absurd conclusions were warmly approved by Lavoisier ; these, and other attacks, were easily repulsed by Black, and his theory was finally accepted by the phlogistonists themselves.

Davy's isolation of the alkali-metals.—Previous to the researches of Davy the caustic alkalies were regarded as elements, although Lavoisier hinted that they might be oxides of unknown metals. Humphry Davy (*b.* 1778—*d.* 1829), whose name is chiefly rememembered for the invention of the safety-lamp, carried out the earliest investigations on electrochemistry. Becoming convinced of the great power of decomposition exhibited by the voltaic battery, and attracted by Lavoisier's conjecture, Davy attempted to decompose the alkalies by electrolysis. The experiment succeeded.

In 1807 he found that : " A small piece of pure potash which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface [by attraction of moisture, and slight deliquescence], was placed upon an insulated disc of platina, connected with the negative side of the battery . . . in a state of intense activity ; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. . . . The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered with a white film which formed on their surfaces. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash."

This metal, which Davy called **potassium,** was found to possess extraordinary properties:

(1) It is lighter than water (density 0·875).

(2) When thrown on water it instantly decomposes it, attracting the oxygen; the liberated hydrogen is ignited by the heat developed, and burns over the rapidly-moving floating globule of metal with a heliotrope-coloured flame. Some of the caustic potash produced dissolves in the water, but a small fused globule is left, which exists in the spheroidal condition, and, on cooling down, dissolves with a sharp crack, often being projected from the surface of the liquid.

(3) The metal rapidly oxidises in the air; a freshly-cut piece, which shows a bright, metallic lustre for an instant, becoming at once covered with a blue tarnish. The metal is therefore preserved under petroleum, which is free from oxygen.

In the same way, from caustic soda, **sodium** was isolated, and by heating these metals with the alkaline earths, lime, strontia, baryta, and magnesia, the metallic bases of the latter were prepared, and called calcium, strontium, barium, and magnesium. Boron was isolated by the action of potassium on fused boric acid. Sodium, like potassium, decomposes water, but, as the heat evolution is not so great, the liberated hydrogen does not take fire unless the sodium is prevented from moving about by placing it on starch-jelly; the hydrogen then catches fire, and burns with a bright yellow flame.

Gay-Lussac and Thenard in 1808 showed that, when molten caustic potash or soda was brought in contact with red-hot iron turnings, the iron was oxidised, and the alkali metal distilled off. At the same time, a considerable amount of hydrogen was evolved. The caustic alkalies were then recognised as **hydroxides,** KOH and NaOH, of the metals potassium and sodium, not, as had been supposed by Davy, the oxides.

Expt. 315.—The presence of hydrogen in caustic potash or soda may be shown by heating a mixture of the powdered alkali with iron filings in a hard glass tube. Hydrogen is evolved, and may be ignited at the mouth of the tube.

Acidic and basic oxides.—Oxides which unite with water to produce acids and bases, respectively, are called **acidic** and **basic oxides** (p. 134).

In some cases, a basic oxide, although forming salts with acids, does not yield an appreciably alkaline solution. This results simply from the small solubility of the oxide, because an indicator such as litmus or phenolphthalein does not react until the hydrogen or hydroxide ions are present in finite, although small, concentrations, the numerical values of which can be determined for each indicator (p. 364).

In the case of **cupric oxide,** for instance, which dissolves readily in dilute sulphuric acid to form cupric sulphate, the solubility in water is so minute that, although the dissolved portion, even in a saturated solution, is practically completely ionised on account of the great dilution (p. 358), yet the total concentration of hydroxide ions never reaches the minimum value required to change the colour of the indicator. The neutralisation with acid, however, follows the normal course, since the solution and ionisation of the base proceeds, as hydroxide ions are removed by the acid: $CuO\ (solid) + H_2O \rightleftharpoons Cu(OH)_2\ (dissd.) \rightleftharpoons Cu^{\cdot\cdot} + 2OH'$.

$$H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4' \rightleftharpoons 2H^{\cdot} + SO_4''.$$
$$H^{\cdot} + OH \rightleftharpoons H_2O.$$

The minute trace of copper oxide dissolved in water is readily detected by its catalytic acceleration of the oxidation of sulphites by atmospheric oxygen (p. 494).

Alumina, Al_2O_3, dissolves both in acids and in alkalies. Aluminium hydroxide is a very weak electrolyte, which can ionise either as an acid or as a base. Both functions are developed simultaneously, since the ionisation in a saturated solution never produces hydrogen and hydroxide ions in excess of the ionisation of water:

$$Al_2O_3\ (solid) + Aq. \rightleftharpoons 2Al(OH)_3(dissd.) \left\{ \begin{array}{l} \rightleftharpoons H^{\cdot} + AlO_2' + H_2O (acid) \\ \rightleftharpoons Al^{\cdot\cdot\cdot} + 3OH'\ (base) \end{array} \right\}$$

Such a substance, exhibiting both acidic and basic functions, which become perceptible in the presence of strong bases and strong acids, respectively, is called an **amphoteric electrolyte.** Its salts with strong acids and strong bases are largely hydrolysed in solution (p. 896).

The composition of salts from acids and bases was first clearly expressed by Tachenius, who says ("Hippocrates chimicus," 1666): "Omnia salsa in duas dividuntur substantias, in alcali et acidum." This was the basis of the dualistic theory (p. 274), and in another form it appears in the modern ionic theory.

SODIUM, Na = 22·82.

The alkali industry.—Sodium carbonate in a very impure form was formerly prepared by burning plants growing on the sea-shore (*Chenopodium, Salicornia, Salsola,* etc.). The plant-ash was called *barilla,* and was used in the manufacture of soap. When Stahl pointed out that the base of common salt is an alkali, attempts were made to obtain soda from this source. An early process was that of Scheele (1773), in which salt is decomposed by boiling with litharge: $2NaCl + 4PbO + H_2O = 2NaOH + PbCl_2,3PbO$. The same chemist also observed that a mixture of lime and salt, when moistened, slowly effloresced, with the formation of sodium carbonate. The preparation of alkali from common salt, however, was first satisfactorily effected by Nicolas Leblanc in 1787. His process comprised the following steps:

(1) **Salt** is converted into **sodium sulphate** by heating with sulphuric acid: $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$.

(2) The sodium sulphate, or *salt-cake* (p. 238), is heated to dull redness with a mixture of **limestone** and powdered **coal,** when **sodium carbonate** and **calcium sulphide** are produced. The reaction probably occurs in two stages:

$$(a)\ Na_2SO_4 + 2C = Na_2S + 2CO_2.$$
$$(b)\ Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The final product is known as *black-ash*; if it is broken up and lixiviated with water, an impure solution of sodium carbonate is obtained, whilst the sparingly soluble calcium sulphide (with excess of coal, limestone, and impurities) remains as *alkali-waste.*

Leblanc established his process in a works by means of a loan from the Duke of Orleans in 1791. Two years later the Duke was guillotined by the friends of liberty and fraternity, and Leblanc's factory was confiscated. The unfortunate inventor, who indeed escaped the fate of his benefactor, lingered on only to die by his own hand in 1806.

After the repeal of the salt tax in England, an alkali works was established in Lancashire, in 1823, by Muspratt, in which the **Leblanc process** was used. During the nineteenth century the Leblanc process was one of the most important British industries, the production of sodium carbonate in the period 1879–1883 being 500,000 tons per annum.

The Leblanc process.—In this process, sulphuric acid, made by the chamber-process from **pyrites,** is heated with **salt** for the production of salt-cake (p. 238), the hydrochloric acid being absorbed and converted into chlorine, which is mostly used in the manufacture of bleaching powder (p. 376). From the burnt pyrites, copper, and sometimes silver and gold, are extracted.

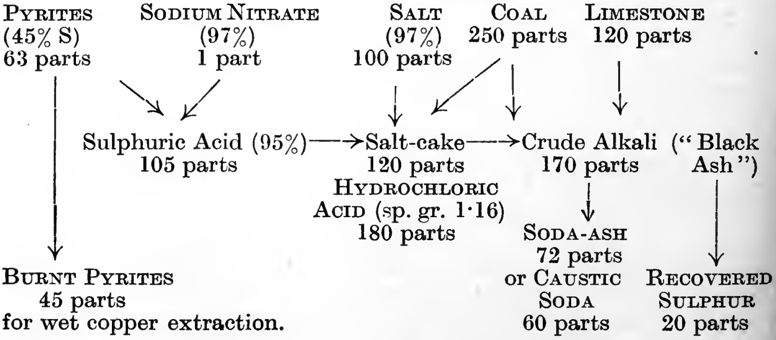
The reduction of the salt-cake with carbon, in the presence of limestone, is carried out in *black-ash furnaces*. At present the product is wholly worked up as **caustic soda,** NaOH, and the operation of making the black-ash is carried out in *revolving furnaces*.

The black-ash revolving furnace, or "revolver," consists (Fig. 381) of a cylinder, *B*, of iron plates lined with firebricks, 15–20 ft. long, running on rollers by means of bands on the outside of the cylinder. The rotation is effected by a cog-wheel passing around the cylinder, which engages with a smaller driving cog-wheel below. The firing is effected by producer gas, made in a generator, *A*, close to the furnace, the flame passing into the revolver through a fireclay ring called the "eye," hung between the end of the furnace and the outlet from the gas generator. The charge consists of 2 tons of salt-cake, 2 tons of crushed limestone, and 1 ton of coal slack, and is introduced in one batch. At first the revolver is turned slowly; it is finally speeded up to 5 or 6 revolutions per minute, and rotation is continued until a yellow flame of carbon monoxide appears. The pasty mass is then discharged into iron trucks through a manhole, about $1\frac{3}{4}$ tons of black-ash being obtained. The waste heat from the furnace is utilised by passing the hot gases over a series of evaporating pans.

The cooled **black-ash** is broken up and lixiviated with water in *Shanks's lixiviating tanks*, operated on the counter-current principle. Fresh water is added to the tank containing nearly spent ash, and the concentrated liquors are used in leaching the freshly added black-ash. The liquors are conveyed from tank to tank by siphon pipes.

The insoluble residue in the lixiviators, the **alkali-waste,** is treated by the Chance-Claus process (p. 476). The liquors contain sodium carbonate, caustic soda, and impurities such as sodium sulphide and iron salts (p. 992); they are worked up directly for the production of caustic soda, this process having been introduced in Lancashire in 1853.

A **diagrammatic scheme of the Leblanc process** is given below,



Caustic soda, NaOH.—The Leblanc liquors (or solutions of sodium carbonate from the ammonia-soda process) are run into *causticisers* (Fig. 382), iron tanks provided with mechanical agitators, and a pipe for admission of steam. Quicklime is placed in an iron cage dipping into the top of the liquor, the stirrer is started, and steam is blown in. The sodium carbonate is practically completely converted into caustic soda :

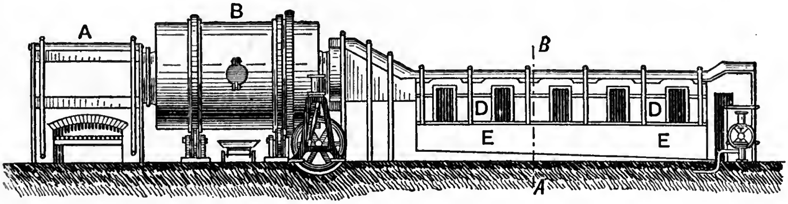


FIG. 381.—Black Ash Revolving Furnace.

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3.$$

Calcium carbonate is slightly soluble, and the dissolved part reacts with caustic soda, converting a portion into sodium carbonate by the reverse reaction. As the concentration of sodium carbonate in the solution decreases, owing to caustification, the solubility of calcium carbonate increases, since the CO_3'' ions of the sodium carbonate, which depress the solubility of the calcium carbonate, are progressively removed. At the same time, the solubility of the calcium hydroxide decreases, since the increasing concentration of hydroxide ions, OH′, of the caustic soda depresses the solubility of the calcium hydroxide. A state of **equilibrium** is reached when the solubilities of the calcium carbonate and calcium hydroxide become equal, since then no further conversion of the one solid phase into the other, brought about by solution of one and the subsequent precipitation of the other solid phase, can occur.

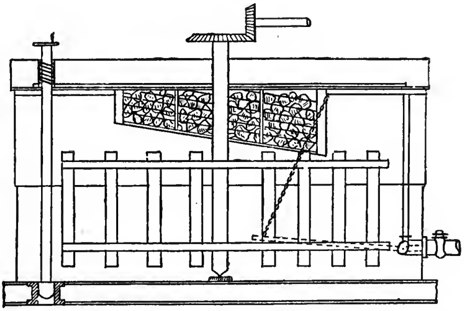


FIG. 382.—Causticiser.

The solubilities of the two solid phases are regulated by the **solubility-product** equations (p. 358):

$$(1)\ Ca(OH)_2\ (\text{solid}) \rightleftharpoons Ca(OH)_2\ (\text{dissd.}) \rightleftharpoons Ca^{\cdot\cdot} + 2OH'$$

$$\therefore\ [Ca^{\cdot\cdot}]_1 \times [OH']^2 = \text{constant} = K_1.$$

$$(2)\ CaCO_3\ (\text{solid}) \rightleftharpoons CaCO_3\ (\text{dissd.}) \rightleftharpoons Ca^{\cdot\cdot} + CO_3''$$

$$\therefore\ [Ca^{\cdot\cdot}]_2 \times [CO_3''] = \text{constant} = K_2.$$

For equilibrium $[Ca^{\cdot\cdot}]_1 = [Ca^{\cdot\cdot}]_2$, *i.e.*, the solubilities of the two solids are equal,

$$\therefore\ \frac{[OH']^2}{[CO_3'']} = \frac{K_1}{K_2} = K.$$

With increasing concentration the equilibrium is shifted from the hydroxide side of the equilibrium equation to the carbonate side, since the concentration $[CO_3'']$ is involved as the first power in the equilibrium constant, whereas the concentration $[OH']$ is involved as the square. Caustification is more complete (99 per cent.) in dilute solutions (normal). The carbonate solution used in practice has a density of 1·1, when 91–92 per cent. of caustification is obtained.

Better results are obtained with strontia or baryta instead of lime, since the hydroxides of strontium and barium are more, and the carbonates less, soluble than those of calcium. Strontia and baryta are too expensive for industrial use.

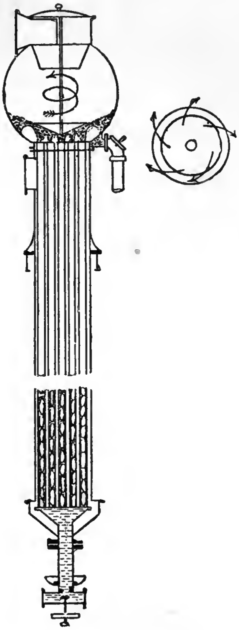


FIG. 383.—Kestner Vacuum Evaporator.

The causticised liquor is next filtered from the lime sludge in a vacuum filter, and concentrated, usually in **vacuum evaporators.** In the latter the liquid is heated by steam coils or jackets under reduced pressure; the boiling point is lowered and steam at a lower temperature than 100° (*e.g.*, exhaust steam) can be employed. One type is the **Kestner evaporator** (Fig. 383), consisting of a series of tubes in an outer jacket heated by exhaust steam. The liquor enters inside the tubes at the bottom, under reduced pressure. It commences to boil, and the foam is projected into a collecting head, where it is given a rotary motion by means of vanes. The concentrated liquor thus separated runs off, whilst the steam passes out, either to a similar apparatus under still lower pressure or to a condenser, where it is condensed by cooling, say with a jet of water. The air from the cooling water is removed by a vacuum pump which maintains the low pressure in the apparatus.

The concentrated solution begins to deposit sodium chloride, carbonate, etc., which are removed, and the clear liquor is finally heated in hemispherical cast-iron *soda-pots* over a free flame until all the water is driven off, and fused **caustic soda** remains. This is ladled out into iron barrels, where it solidifies.

In the case of Leblanc soda, a little sodium nitrate is added to the fused charge, to oxidise sulphides and cyanides. Graphite is formed from the latter.

For laboratory purposes the caustic soda is fused and cast into sticks, or powdered. The latter form is usually purer, and is more convenient for use.

In purifying commercial caustic soda (or potash) containing chloride, carbonate, and sulphate, it is warmed with alcohol. The impurities do not dissolve, and the solution is decanted into a silver dish, evaporated, and the residue fused (Berthollet). This material is sold as *pure by alcohol.* It may contain sodium nitrite, and sodium acetate, formed from the alcohol during the evaporation. The purest caustic soda is made from metallic sodium. A piece of sodium which has not been kept under oil is squeezed through a sodium press into distilled water, previously boiled and cooled, contained in a silver dish. The sodium wire should be lowered *slowly* into the water, so that pieces do not become detached. The solution is evaporated and the residue fused.

Caustic soda is a white, slightly translucent, solid with a fibrous texture. It fuses at 310°, and at about 1300° it dissociates into its elements : $2NaOH \rightleftharpoons 2Na + H_2 + O_2$. When exposed to the air, it first deliquesces from absorption of moisture and a little carbon dioxide, forming a saturated solution. The latter, however, slowly resolidifies from absorption of carbon dioxide, when the sparingly soluble bicarbonate, $NaHCO_3$, is formed. (Caustic potash does not resolidify, since potassium bicarbonate is readily soluble. For this reason a concentrated solution of caustic potash is used in gas analysis to absorb carbon dioxide, since it does not deposit solid, which would choke the apparatus.) Caustic soda is a powerful cautery, breaking down the proteins of the skin and flesh to a pasty mass.

Several hydrates of caustic soda, *e.g.*, $NaOH,H_2O$, m.-pt. 64° ; $NaOH,2H_2O$, m.-pt. 12°, have been described.

The chief use of caustic soda in commerce is in the manufacture of **soap** (p. 206). Fats are boiled with caustic soda until hydrolysis has occurred, and the soap, which consists of sodium salts of the fatty acids, is separated by adding salt (" salting out "), when it rises to the surface, is removed, pressed, and cut into bars.

The ammonia-soda process.—In 1838 Dyar and Hemming proposed to make sodium carbonate from common salt by precipitating a concentrated solution of the latter with ammonium hydrogen carbonate, when sodium hydrogen carbonate (" sodium bicarbonate," or " bicarbonate of soda ") separates out :

$$NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl.$$

This **ammonia-soda process** was worked on a technical scale by Schloesing and Rolland, from whose paper (1855) the following account of the chemistry of the process is taken. Of the multitude of types of apparatus described in Solvay's later patents, practically only the carbonating tower (p. 783) is still in use ; even this is not essential. The ammonia-soda process was introduced by John Brunner and Robert Mond, in 1874, at Winnington, near Northwich, in Cheshire, and in 1904 the works of Brunner, Mond and Co. converted 1,703,805 tons of salt into sodium carbonate. The Leblanc industry steadily declined, and in 1908, out of a total world's production of 2 million tons of soda, only 100,000 tons were made by the older process. Another severe blow was given to the Leblanc process by the introduction of **electrolytic methods** in 1895 (Chapter XVI).

The **raw materials** for this process are common salt (or brine), limestone, coal, and ammonia. It consists of a cycle of **six operations,** which are carried on continuously day and night :

(1) A solution of salt is prepared, containing 31 per cent. of NaCl, ammonia, and ammonium carbonate, freed from the calcium and iron, and most of the magnesium, salts of the original brine.

(2) This ammoniacal brine is treated with carbon dioxide, which first converts the ammonia into carbonate :

$$\text{(i)}\ 2NH_3 + H_2O + CO_2 \rightleftharpoons (NH_4)_2CO_3,$$

and then tends to convert this into bicarbonate :

$$\text{(ii)}\ (NH_4)_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NH_4{\cdot}HCO_3.$$

In proportion as ammonium bicarbonate is formed it reacts with the sodium chloride, giving by double decomposition **sodium bicarbonate,** $NaHCO_3$, and ammonium chloride :

$$\text{(iii)}\ NH_4{\cdot}HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl.$$

The former salt is only slightly soluble in brine, and is nearly all precipitated, whilst the latter remains in solution. Only two-thirds of the common salt is converted into sodium bicarbonate, since the reaction is reversible, and one-third of the salt and of the ammonium bicarbonate remain. The mother liquor, which passes to the ammonia-stills, therefore contains one-third of its ammonia " volatile " and two-thirds " fixed " (p. 550).

(3) The bicarbonate is filtered, and washed so as to free it as far as possible from ammonium salts.

(4) The bicarbonate is ignited to produce sodium carbonate and nearly pure carbon dioxide (" roaster CO_2").

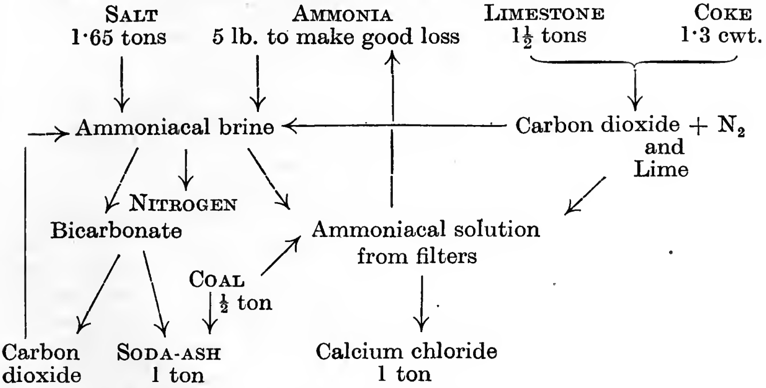
(5) The ammoniacal salt solutions from (2) and (3) are treated in

stills with steam and lime to set free the ammonia, and form calcium chloride.

(6) Limestone is burnt to produce carbon dioxide diluted with nitrogen (" limekiln CO_2"), and the lime required for operation (5).

The **products** of the process are nearly pure sodium carbonate, nitrogen containing a little carbon dioxide, and a solution of calcium chloride. The two latter are waste-products.

A diagrammatic scheme of the ammonia-soda process is given below



The operations are carried out as follows. The brine is saturated with ammonia gas from the stills, and the precipitated impurities ($CaCO_3$, $MgCO_3$, $Fe(OH)_3$) allowed to settle. The ammoniacal brine is then pumped through pipes to the iron **carbonating towers** (Fig. 384), 6ft. in diameter and 70-90ft. high, provided with perforated inverted bubblers, as shown. Carbon dioxide (obtained by mixing the roaster and limekiln gases) is pumped in below through the distributer, *b*, and bubbles through the ammoniacal brine in the tower, forming a sludge of bicarbonate which runs off to the **filters** from *e*. The liquor from the filters, containing all the ammonium salts, passes to the **ammonia-stills,** where it is treated with steam and lime in the usual way (p. 551), forming ammonia gas (with some carbon dioxide), which is used in the preparation of ammoniacal brine, and a solution of calcium chloride, which is a waste product (containing the lime used, and the chlorine of the salt). The sodium bicarbonate from the filters is then calcined in closed tubular **calcining pans,** fitted with scrapers which push the solid along the pan. Carbon dioxide is evolved: $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$. This gas is mixed with the scrubbed gas from the **limekilns,** where the limestone is burnt mixed with coke (p. 841), and passed to the carbonating towers. Sodium carbonate, or **soda-ash**, issues from

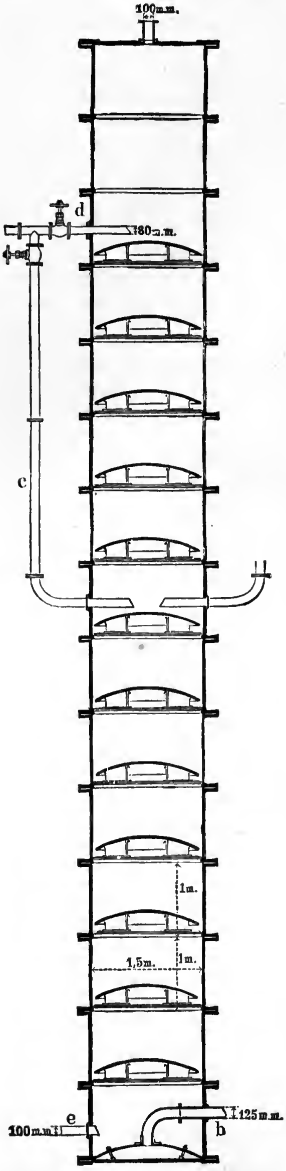


FIG. 384.—Carbonating Tower of Ammonia-Soda Process.

the calcining pan. This is nearly pure; it usually contains only a little sodium chloride, derived from the mother liquor left in the bicarbonate on the filters.

From the soda-ash of the ammonia-soda works, various products may be made. **Washing-soda,** $Na_2CO_3,10H_2O$, is obtained by dissolving in hot water and crystallising. **Crystal carbonate,** Na_2CO_3,H_2O, is formed by evaporation, and separates from the hot solution. **Concentrated soda crystals,** $Na_2CO_3,NaHCO_3,2H_2O$, are produced by crystallising a hot solution of equimolecular amounts of carbonate and bicarbonate.

Caustic soda is made by boiling the solution of the carbonate with lime, as already described, or by the **Löwig process.** In the latter, a mixture of soda-ash and ferric oxide is heated to bright redness in a revolving furnace, when **sodium ferrite,** Na_2O,Fe_2O_3, or $NaFeO_2$, is formed:

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2.$$

The mass is cooled, broken up, and thrown into hot water, when hydrolysis of the ferrite, with formation of caustic soda and insoluble ferric oxide, which is used again, occurs:

$$2NaFeO_2 + H_2O = Fe_2O_3 + 2NaOH.$$

The caustic soda solution is concentrated in vacuum evaporators, and finally heated in soda-pots (p. 781) over a free fire to produce fused caustic soda, which is ladled into iron drums.

Sodium carbonate, Na_2CO_3.—Anhydrous sodium carbonate, known as **soda-ash,** is a white amorphous powder, which aggregates on exposure to moist air, owing to the formation of hydrates. It melts at 852°. When added to water, a considerable amount of heat is evolved, and the hydrated salt is formed usually as an agglomerated mass, which then dissolves slowly. The solution is distinctly alkaline, owing to hydrolysis: $Na_2CO_3 \rightleftharpoons 2Na^{\cdot} + CO_3''$; $CO_3'' + H_2O \rightleftharpoons HCO_3' + OH'$. In $0{\cdot}1N$ solution, 3·17 per cent. of the salt is hydrolysed, *i.e.*, from every 100 molecules of Na_2CO_3 dissolved, 3·17 molecules of NaOH are formed. The solution slowly loses carbon dioxide on boiling.

On evaporating the solution, and cooling, large monoclinic crystals of **washing-soda,** $Na_2CO_3,10H_2O$, are deposited. These effloresce in the air, forming a white powder of the monohydrate Na_2CO_3,H_2O, which is also formed from the decahydrate at 35·1°. This form is deposited from hot solutions, and is known as *crystal carbonate*; it occurs native in the soda lakes of Egypt. Other hydrates, *e.g.*, $Na_2CO_3,7H_2O$, are known.

Sodium bicarbonate, $NaHCO_3$.—This salt is produced in large quantities by the ammonia-soda process, but is all converted into carbonate, the bicarbonate of commerce being prepared from the latter. A concentrated solution, or moist crystals, of sodium carbonate give, when saturated with carbon dioxide, a white crystalline precipitate of bicarbonate. This may be washed with a little cold water, in which it is sparingly soluble, and dried in the air: $CO_3'' + CO_2 + H_2O \rightleftharpoons 2HCO_3'$. The precipitation is due to the fact that, in concentrated solutions, the solubility-product (p. 358), $[Na^{\cdot}] \times [HCO_3']$, of the salt is readily exceeded. The precipitated bicarbonate is easily freed by washing from impurities contained in the original carbonate (*e.g.*, NaCl), since these are readily soluble, and if it is gently ignited in a platinum crucible, **pure sodium carbonate** is produced, which may be used as a standard in volumetric analysis: $2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2$. The solution of the bicarbonate is slightly hydrolysed, and has an alkaline reaction, though this is much feebler than that of the carbonate: $HCO_3' + H_2O \rightleftharpoons OH' + H_2CO_3$. On heating the solution, bubbles of carbon dioxide are evolved: $H_2CO_3 \rightleftharpoons H_2O + CO_2$. By prolonged boiling, practically all the bicarbonate is converted into carbonate, and if crude bicarbonate from the ammonia-soda process is boiled with water, the ammonium salts are expelled as well. On recarbonating, almost pure sodium bicarbonate is precipitated, and the commercial salt is made in this way.

Sodium sesquicarbonate, $Na_2CO_3,NaHCO_3,2H_2O$.—If equimolecular amounts of sodium carbonate and sodium bicarbonate are dissolved in warm water, and the solution cooled to 35°, monoclinic crystals of **sodium sesquicarbonate,** $Na_2CO_3,NaHCO_3,2H_2O$, are deposited. This salt occurs naturally as *trona*, or *urao*, in various localities, and is produced by the spontaneous evaporation of soda lakes. The artificial salt, known as *concentrated soda crystals*, is used in wool-washing. It is neither efflorescent nor deliquescent.

Large deposits of sesquicarbonate occur at Magadi, in British East Africa, and are worked by the Magadi Soda Company.

Metallic sodium.—Although first prepared (Davy, 1807) from caustic soda by electrolysis :

$$\begin{array}{ccccc} & & 2NaOH & & \\ & \swarrow & & \searrow & \\ (-)\ 2Na \leftarrow 2Na^{\cdot} & & & & 2OH' \rightarrow H_2O + O\ (+) \\ \uparrow & & & & \downarrow \\ 2\epsilon & & & & 2\epsilon \end{array}$$

metallic sodium was for many years produced on the large scale by a process due to Castner (1886). In this, caustic soda was heated to 1000° in iron retorts with crude carbide of iron, prepared by heating pitch with spongy iron from the reduction of pyrites-cinder with water gas : $6NaOH + 2C = 2Na + 3H_2 + 2Na_2CO_3$. In 1891 Castner, on account of the developments in the economical generation of electricity, was able to revert to Davy's original process, and all the sodium of commerce (about 5000 tons per annum) is now produced by this method.

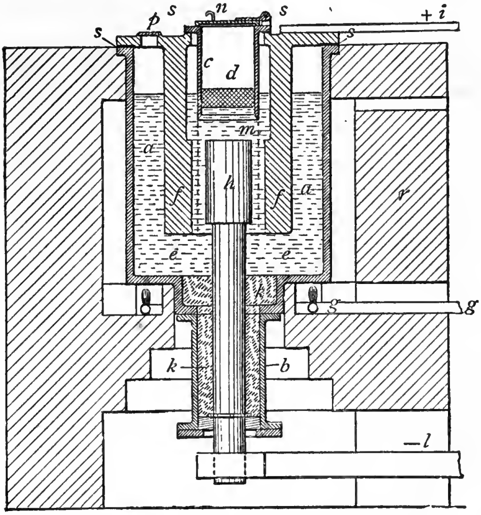


FIG. 385.—Manufacture of Sodium by Electrolysis.

The electrolysis of sodium chloride, mixed with potassium or calcium chloride, or sodium fluoride, is also carried out.

The caustic soda is fused in a cylindrical iron pot (Fig. 385), and maintained at a temperature not higher than 330° by a ring of gas-burners, *g*. A cylindrical iron cathode, *h*, passes up through the base, and is sealed by solidified caustic soda, *k*, into a prolongation, *b*, of the pot. The anode is a cylinder of nickel, *f*, and is in electrical connection with a wire gauze cylinder, *m*, surrounding the cathode. The metal rises from the cathode, and floats at *d* on the surface of the caustic soda inside a small metal receptacle, *c*, provided with a lid, *n*. It is removed by a wire gauze spoon, which allows the fused caustic soda to flow away, but retains the sodium. The latter is sent out, sealed up in tin cans, in the form of thick rods. This process is carried out by the Castner-Kellner Co. at Newcastle, and at Clavaux (France); by the Niagara Electrochemical Co. in America; and by the Elektrochemische Fabrik Natrium at Rheinfelden, in Germany. The metal is used in the preparation of cyanides, sodium peroxide, silicon, magnesium, and organo-metallic compounds in the dye industry.

Sodium is a silver-white soft metal, which may be obtained in octahedral crystals on slow cooling of fused sodium. A colloidal solution in ether has the same violet colour as the vapour. The clean, freshly-cut surface of the metal rapidly tarnishes in the air, a green phosphorescence being visible in the dark. The metal burns when heated in oxygen or chlorine, but may be distilled unchanged in the perfectly dry gases. It acts violently on water: $2Na + 2H_2O = 2NaOH + H_2$ (p. 181). Sodium is a good conductor of electricity; its conductivity is about 36 per cent. that of silver (the best conductor).

Oxides of sodium.—Two oxides of sodium are known: **sodium monoxide,** Na_2O, a basic oxide, and **sodium peroxide,** Na_2O_2, or $Na{\cdot}O{\cdot}O{\cdot}Na$.

Sodium monoxide is obtained either by burning sodium at 180° in a limited supply of air or oxygen and distilling off the excess of metal in a vacuum, or by heating sodium peroxide, nitrate, or nitrite with sodium: $2NaNO_3 + 10Na = 6Na_2O + N_2$. It is a white amorphous mass, which decomposes at 400° into the peroxide and metal. It reacts violently with water: $Na_2O + H_2O = 2NaOH$, but does not absorb carbon dioxide at the ordinary temperature.

Sodium peroxide, Na_2O_2, is produced when the metal burns in excess of air or oxygen, and is manufactured by heating sodium in aluminium trays in a current of purified air at 300° in iron pipes, about 500 tons being produced annually. Sodium peroxide is a yellow substance, becoming white on exposure to air from formation of sodium hydroxide and bicarbonate. When very strongly heated, it evolves oxygen. An aqueous solution may be prepared by adding the powder in small quantities at a time to a well-stirred mixture of ice and water, a crystalline hydrate, $Na_2O_2,8H_2O$, being formed. The liquid is strongly alkaline, owing to hydrolysis: $Na_2O_2 + 2H_2O \rightleftharpoons 2NaOH + H_2O_2$. On warming, oxygen is evolved. Carbon dioxide decomposes sodium peroxide with evolution of oxygen, hence the solid has been used for purifying air in confined spaces (*e.g.*, in submarines). The solution is an oxidising agent, *e.g.*, it converts chromic hydroxide into sodium chromate; and the fused salt shows powerful oxidising properties, converting chrome-ironstone (FeO,Cr_2O_3) into ferric oxide and soluble sodium chromate.

Expt. 316.—A little sodium peroxide mixed with sawdust is placed on filter-paper and moistened with water: the mass inflames. If mixed with pieces of recently ignited charcoal and heated in a covered porcelain crucible to 300–400°, a violent reaction occurs, and metallic sodium condenses on the lid of the crucible: $3Na_2O_2 + 2C = 2Na_2CO_3 + 2Na$. Glacial acetic acid inflames when the peroxide is dropped into it.

If sodium peroxide is treated with absolute alcohol at 0°, a white powder of **sodyl hydroxide,** or **sodium hydrogen peroxide,** $Na{\cdot}O{\cdot}O{\cdot}H$, is formed: $Na_2O_2 + EtOH = NaOEt + NaO{\cdot}OH$. It explodes on heating, evolving oxygen, and forming caustic soda. A stable compound, $2NaO_2H,H_2O_2$, is formed on mixing 30 per cent. hydrogen peroxide with sodium ethoxide (NaOEt) and absolute alcohol. By the action of an ethereal solution of H_2O_2 on sodium, a white solid, $2NaHO_2,H_2O_2$, is obtained. Potassium forms $2KHO_2,H_2O_2$.

Sodium hydride, NaH.—Sodium hydride is prepared by passing a slow stream of dry hydrogen over sodium in a nickel boat, heated in a glass tube to 365°. Colourless matted crystals form on the upper cooler portion of the tube just beyond the boat. These are decomposed by water, with evolution of hydrogen: $NaH + H_2O = NaOH + H_2$. Sodium hydride is not acted upon by concentrated sulphuric acid. At 430° it dissociates rapidly: $2NaH \rightleftharpoons 2Na + H_2$. It absorbs carbon dioxide, producing sodium formate: $NaH + CO_2 = Na{\cdot}CO{\cdot}OH$.

Sodium cyanide, NaCN (or NaCy).—This salt is formed by adding hydrocyanic acid to caustic soda: $NaOH + HCN \rightleftharpoons NaCN + H_2O$, and by heating sodium ferrocyanide, alone or with sodium: $Na_4Fe(CN)_6 = 4NaCN + Fe + 2C + N_2$; $Na_4Fe(CN)_6 + 2Na = 6NaCN + Fe$. The pure cyanide is precipitated by passing hydrocyanic acid into an alcoholic solution of caustic soda. Sodium cyanide is made on a large scale by **Castner's process;** ammonia is passed over sodium heated in iron retorts to 300–400°, and the fused sodamide produced is poured over red-hot charcoal, when **sodium cyanamide,** $Na_2{:}N{\cdot}CN$, is formed. This reacts with the heated charcoal, forming sodium cyanide:

$$\begin{aligned} 2Na &+ 2NH_3 &&= 2NaNH_2 + H_2. \\ 2NaNH_2 &+ C &&= CN{\cdot}N{:}Na_2 + 2H_2 \\ CN{\cdot}N{:}Na_2 &+ C &&= 2NaCN. \end{aligned}$$

Sodium cyanide is hydrolysed in aqueous solution; the latter is alkaline, and smells of hydrocyanic acid: $NaCN + H_2O \rightleftharpoons NaOH + HCN$.

Sodium in analysis.—Sodium compounds give an intense yellow flame when heated on platinum wire in the Bunsen flame. The light, on examination by the spectroscope, shows two yellow lines, very close together, constituting what is known as the double D-line; their wave-lengths are 5896 and 5890 Å.U. This spectrum is given by practically every solid heated in the flame, since sodium is very widely distributed in Nature. White, sparingly soluble, precipitates of the sodium salts are formed when potassium pyroantimoniate (p. 935) or potassium dihydroxytartrate are added to fairly concentrated solutions of sodium compounds.

POTASSIUM, $K = 38{\cdot}79$.

Potassium compounds.—Potassium occurs much less abundantly than sodium, although it is widely distributed throughout the three kingdoms of Nature. **Primary rocks** often contain potassium silicate; thus granite contains 1·7 to 3·1 per cent. of potassium, mainly in the form of *orthoclase felspar* (p. 891): $K_2O,Al_2O_3,6SiO_2$. *Potash mica*, or *muscovite*, has the formula $(KH)_2Al_3(SiO_4)_3$. During the **weathering** of these rocks, *i.e.*, their decomposition by atmospheric carbon dioxide and water, assisted by the disintegrating action of frost, the silicates are decomposed into clay and soluble potassium salts, such as potassium carbonate. The latter are retained by a process of adsorption in the **soil**, where they remain available for absorption by the roots of plants (p. 696). The mechanism of the selective retention of potassium salts by the soil appears to depend on the exchange of potassium for sodium in *zeolites*, or hydrated silicates:

$$Na_2O,Al_2O_3,3SiO_2,2H_2O \ (\textit{natrolite}) + 2KOH \rightleftharpoons K_2O,Al_2O_3,3SiO_2,2H_2O + 2NaOH.$$

In **plants**, potassium compounds occur as salts of organic acids: *e.g.*, sorrel and rhubarb contain **acid potassium oxalate**, $KHC_2O_4,H_2C_2O_4,2H_2O$, "salt of sorrel," or "salts of lemon," used to remove ink-stains from linen; and grape-juice contains **acid potassium tartrate**, $KHC_4O_4O_6$, "cream of tartar," or "argol." When plants are burnt, these organic salts form **potassium carbonate**, K_2CO_3, which, since it was formerly prepared by calcining cream of tartar, received the name *salt of tartar*. Large amounts of potassium carbonate are made in Canada, Transylvania, and Russia, by lixiviating wood ashes with water, evaporating the solution to dryness, and calcining the residue in iron pots. The product is *pot-ash*; when purified it is known as *pearlash*.

According to Dyer (1894), the minimum amount of soluble potash (K_2O) in a fertile soil is 0·01 per cent.; the mean available potash content of British soils is 0·015 per cent. If successive crops are grown on the soil, the potassium compounds are removed, and the soil becomes infertile. Trees remove annually 1·25 lb. of K_2O per acre, other plants more (p. 696). This exhaustion of the soil is occurring in America, where the wheat-growing areas are moving further and further west. In order to keep up the fertility of the soil, potassium compounds must be supplied; they are therefore essential as **fertilisers.**

The interesting suggestion has been made that the occurrence of potassium compounds in plants, and the fact that the latter cannot grow without potassium compounds, are connected with the feebly radioactive properties of this element. The metal emits β-rays, but its activity is only one-thousandth that of uranium. Radioactive substances are said to promote plant growth even in the absence of potassium salts.

Plants serve as food for **animals,** and the blood serum of all animals contains 0·022 per cent. of potassium and 0·32 per cent. of sodium. In the milk of carnivora, sodium and potassium occur in approximately equivalent amounts; in that of herbivora, and in human milk, potassium predominates (6 : 1). The perspiration of the sheep is rich in potassium salts of the organic **sudoric acid.** If raw wool is washed with water, the brown liquid evaporated, and the residue calcined, about 5 parts of potassium carbonate remain per 100 of wool. This is a limited source of potassium salts.

Potassium salts occur in the **sea,** and are absorbed in marine plants, from the ashes of which (*kelp*) they may be extracted. Sugar beets absorb from the soil considerable amounts of potassium salts, which accumulate in the molasses, known as *vinasse*, or *schlempe.* They are evaporated on open hearths, and splashed by paddles in the fire gases (Porion furnace); the syrup burns, leaving a residue of potassium carbonate. The vinasse may also be distilled in iron retorts, when methyl chloride and trimethylamine are formed.

Deposits of potassium salts.—Although potassium salts are widely distributed, *e.g.*, as felspar, comparatively few workable deposits of salts occur. The principal deposits are found at Stassfurt, in Saxony; at Mulhouse, in Alsace; at Cardona, in Spain; and, in lesser amounts, in Eastern Galicia, Searle's Lake (Nebraska), and Elton Lake, in the Urals.

The **Stassfurt potash deposits** held, until quite recently, the monopoly of the world's supply. They were discovered in boring for rock-salt in 1839, and are of great thickness. The arrangement of the deposits is as follows:

Top.

Alluvial and diluvial deposits.
"Bunter" sandstone—Triassic formation (600–800 ft. thick).
Gypsum, anhydrite, red clay, etc.
Newer common salt (a later formation, often lacking).
Anhydrite.
"Salzthon" (three layers: bottom, of gypsum; middle, of magnesia and alumina; top, of clay containing 40 per cent. of $MgCO_3$, protecting the lower deposits).

Carnallite region, chiefly $KCl,MgCl_2,6H_2O$ (50–130 ft. thick).

Kieserite region (chiefly $MgSO_4,H_2O$)—" Abraum " salts, *i.e.*, *above* common salt.

Polyhalite region—mixed salts.

Older common salt (2000 ft.).

Anhydrite.

Bituminous sandstone.

The deposits are probably derived from the evaporation of an inland lake, as the order of the successive layers of salts is what would be expected in such a case (Van't Hoff).

The chief source of potassium salts in the Stassfurt deposit is the double salt **carnallite,** $KCl,MgCl_2,6H_2O$, which contains, when pure, 14·1 per cent. of potassium. The Alsatian and Galician deposits contain *sylvine,* an isomorphous mixture of sodium and potassium chlorides, richer in potassium than carnallite. The *kainite,* $K_2SO_4,MgSO_4,6H_2O$, of Stassfurt is not worked to any extent.

Potassium carbonate.—In the preparation of potassium salts from carnallite, the latter may be fused, when nearly pure potassium chloride separates, leaving fused hexahydrate of magnesium chloride: $KCl,MgCl_2,6H_2O \rightleftharpoons KCl + MgCl_2,6H_2O$. The potassium chloride is recrystallised. Usually, the carnallite is treated with mother-liquor from the crystallisations. On heating the paste of potassium chloride and the saturated solution of magnesium chloride, formed by the action of water on the double salt, a clear solution is obtained, from which on cooling 80 per cent. of the potassium chloride is deposited. From the chloride the sulphate and carbonate are prepared by a modification of the Leblanc process. The charge for the black-ash furnace (p. 778) consists of 100 parts of K_2SO_4, 80–90 parts of limestone, and 40–50 parts of coal.

Potassium chloride is also converted into carbonate by **Precht's process.** A concentrated solution is mixed with solid hydrated magnesium carbonate, and carbon dioxide (limekiln gas) passed through. A solid of the composition $MgCO_3,KHCO_3,4H_2O$ and a solution of magnesium chloride are formed: $3(MgCO_3,3H_2O) + 2KCl \text{ aq.} + CO_2 = 2(MgCO_3,KHCO_3,4H_2O) + MgCl_2 \text{ aq.}$

This solid is heated to 140° with water under pressure. A solution of potassium carbonate, a precipitate of magnesium carbonate, and carbon dioxide gas are formed:

$$2(MgCO_3,KHCO_3,4H_2O) = 2MgCO_3 + K_2CO_3 + 9H_2O + CO_2.$$

Potassium carbonate, K_2CO_3 (*pearlash*), is a white deliquescent powder, dissolving readily in water to form a strongly alkaline solution: $K_2CO_3 + H_2O \rightleftharpoons KHCO_3 + KOH$.

One hundred parts of the water dissolve:

	0°	26°	40°	60°	80°	135° (b.-pt. sat. sol.)
K_2CO_3	105	113·5	117	127	140	205

It fuses at 879°, but melts at a lower temperature when mixed with sodium carbonate—**fusion mixture**, and loses carbon dioxide when heated to redness in steam: $K_2CO_3 + H_2O = 2KOH + CO_2$.

A crystalline hydrate, $K_2CO_3,2H_2O$, is stable in contact with water from − 7° to 135°. The concentrated solution on standing deposits monoclinic crystals of $2K_2CO_3,3H_2O$, which at 100° fall to a white powder of K_2CO_3,H_2O, and at 130° yield the anhydrous salt.

Potassium carbonate solution readily absorbs carbon dioxide, and a saturated solution on cooling deposits monoclinic crystals of **potassium hydrogen carbonate,** or "potassium bicarbonate," $KHCO_3$ (or $K_2O,2CO_2,H_2O$), which is easily prepared by passing carbon dioxide over moistened potassium carbonate and drying on a porous plate. The salt is much less soluble in water than the normal carbonate. One hundred parts of water dissolve at 10°, 27·7, and at 60°, 60 parts of K_2CO_3.

The recrystallised bicarbonate may be used in preparing pure potassium carbonate, since it decomposes at 190°: $2KHCO_3 \rightleftharpoons K_2CO_3 + H_2O + CO_2$. The properties of the solution are similar to those of sodium bicarbonate (p. 785).

Potassium hydroxide, or caustic potash, KOH.—**Caustic potash** is prepared in a similar manner to caustic soda, which it resembles closely in its properties (p. 781). It is made on the large scale by the electrolysis of a solution of potassium chloride, and is used in the manufacture of **soft-soap** (potassium salts of oleic, palmitic, and stearic acids). The pure hydroxide is prepared by the action of barium hydroxide on potassium sulphate: K_2SO_4 (powder) $+ Ba(OH)_2$ (hot saturated solution) $\rightleftharpoons BaSO_4$ (pp.) $+ 2KOH$, or by the action of water on potassium amalgam. It forms a crystalline hydrate, $KOH,2H_2O$, m.-pt. 35·5°, although solutions containing more than 85 per cent. deposit KOH on cooling. The solutions attack glass, and should be decanted (not filtered), and evaporated in silver, nickel, or iron dishes. Platinum is attacked by fused alkalies.

Potassium chloride, KCl.—This salt occurs in cubic crystals as *sylvine*. It melts at 790°, and is easily soluble in water, the solubility increasing from 28 at 0° to 32·7 at 15° and 56·5 at 100° almost linearly with temperature (*cf.* Fig. 68). The salt is made from carnallite, as previously described, and is used as a fertiliser.

The **bromide,** KBr, and **iodide,** KI, are prepared as previously described (p. 395); they form cubical crystals, which melt at 750° and 705° respectively, and are used in medicine and photography. The **fluorides,** KF, KHF_2, KH_2F_3, and KH_3F_4 are known.

Potassium phosphate, K_3PO_4, is formed by heating a phosphate, or phosphatic slag (p. 981), with coke and potassium sulphate, and is used as a fertiliser.

A **phosphide,** K_2P_5, is obtained by heating the elements at 400° in an exhausted tube. The compounds Na_2P_5, Rb_2P_5, and Cs_2P_5 are similarly obtained.

The **metaborate,** KBO_2, is prepared by fusing K_2CO_3 with B_2O_3; on adding potash to boric acid till the solution is alkaline, a **pyroborate,** $K_2B_4O_7,5H_2O$, is formed. By mixing H_3BO_3 and $2K_2CO_3$ in hot solutions, a **triborate,** $2KB_3O_5,5H_2O$, is formed, whilst the **pentaborate,** $KB_5O_8,4H_2O$, is made by saturating hot caustic potash solution with boric acid.

By adding cold 3 per cent., and 30 per cent., H_2O_2, respectively, to a saturated solution of the metaborate, two **perborates,** $2KBO_3,H_2O$ and $2KBO_3,H_2O_2$, are obtained.

Potassium in analysis.—Potassium forms sparingly soluble salts with perchloric, fluosilicic, chloroplatinic, tartaric, and picric acids, all of which, together with sodium cobaltinitrite (p. 1001), may be used as reagents for the potassium ion. The potassium hydrogen tartrate is precipitated only in solutions containing no mineral acid; its precipitation (as well as that of the chloroplatinate) is facilitated by adding alcohol, and scratching the tube with a glass rod. The purple flame coloration and the spectrum are also useful as tests.

Potassium cyanide, KCN.—Potassium cyanide is formed by heating the ferrocyanide alone at a bright red heat: $K_4Fe(CN)_6 = 4KCN + Fe + 2C + N_2$, or with potassium carbonate: $K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO$ (cyanate) $+ CO_2 + Fe$. If the ferrocyanide is fused with sodium, a mixture of sodium and potassium cyanides is formed:

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

Potassium cyanide is now prepared by **Beilby's process;** a mixture of fused potassium carbonate and carbon is treated with ammonia gas: $K_2CO_3 + C + 2NH_3 = 2KCN + 3H_2O$. The fused cyanide is decanted and moulded, and is quite pure. The **cyanate,** KCNO, or CO:NK, is obtained by fusing the cyanide with lead oxide: $KCN + PbO = KCNO + Pb$ (the cyanide is a powerful **reducing agent**), or by heating the ferrocyanide and potassium dichromate in an iron dish, and extracting with 80 per cent. alcohol. The aqueous solution slowly hydrolyses, with formation of ammonia:

$$KCNO + 2H_2O = NH_3 + KHCO_3.$$

The **thiocyanate,** KCNS, is formed by fusing a mixture of potassium ferrocyanide and carbonate, with sulphur. It occurs in traces in saliva. **Potassium hydride,** KH, is formed similarly to the sodium compound.

Potassium.—The metal is prepared in a similar way to sodium by the electrolysis of fused caustic potash.

EXPT. 317.—It may be obtained on a small scale by electrolysing a fused mixture of equimolecular proportions of potassium chloride and calcium chloride in a porcelain crucible, provided with two carbon electrodes, and heating with a Bunsen burner placed on the anode side, so that a solid crust forms over the cathode (Fig. 386). If six to eight accumulators are used, a globule of potassium forms under the crust. The whole is cooled, and opened up under petroleum.

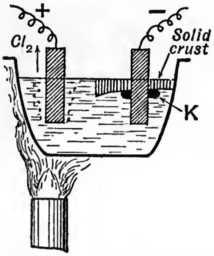


FIG. 386.—Preparation of Potassium by Electrolysis.

Metallic potassium was formerly prepared by heating a mixture of the carbonate with charcoal to whiteness in iron bottles, and cooling the vapour rapidly in flat condensers: $K_2CO_3 + 2C = 2K + 3CO$. Unless the cooling was very rapid, combination of potassium with carbon monoxide occurred, with the formation of a yellow compound, $C_6O_6K_6$, which is a salt of hexahydroxybenzene, $C_6(OH)_6$. On exposure to moist air, this forms very explosive substances.

Potassium can also be prepared by the electrolysis of potassium cyanide, by heating caustic potash or potassium sulphide with iron, magnesium, or aluminium, or by heating calcium carbide with potassium fluoride. It comes into the market in small spheres, preserved under petroleum.

Potassium is a very soft metal, with a silver-white colour. It is not acted upon by perfectly dry oxygen, but is rapidly corroded in moist air (*cf.* Na), becoming covered at first with a blue film. It acts violently on water, the liberated hydrogen burning with a purple flame (p. 775). When heated with practically every gas containing oxygen, it abstracts the latter; it also decomposes the oxides of boron and silicon, and the chlorides of magnesium and aluminium, on heating, with liberation of the elements. The metal also occurs in traces in blue specimens of sylvine, which also contain small quantities of helium and neon.

Oxides of potassium.—**Potassium monoxide,** K_2O, is prepared in a similar manner to Na_2O (p. 787), and has similar properties. **Potassium tetroxide,** K_2O_4, is obtained as a chrome-yellow solid by burning the metal in oxygen or air (Gay-Lussac and Thenard), or by the action of ozone on solid caustic potash: $2KOH + O_3 = K_2O_4 + H_2O$. It oxidises carbon monoxide to dioxide below 100°; with water it forms H_2O_2, KOH, and oxygen. A **dioxide,** K_2O_2, is said to be formed when K_2O_4 is exposed to moist air.

Potassium and sodium sulphides.—Potassium and sodium burn when heated in sulphur vapour, forming mixtures of sulphides. The **monosulphides,** Na_2S and K_2S, are obtained by passing hydrogen over the heated sulphates, and, in a less pure form, by heating the sulphates with excess of carbon: $K_2SO_4 + 2C = K_2S + 2CO_2$. By fusing potassium carbonate with sulphur, a liver-coloured mass is obtained, known as **liver of sulphur** (*hepar sulphuris*). It contains polysulphides of potassium, together with potassium sulphate and thiosulphate. A solution of liver of sulphur is used in gardening to combat mildew and insect pests.

If a solution of caustic potash or soda is saturated with sulphuretted hydrogen, and evaporated, the **hydrosulphides,** $NaHS,2H_2O$ or $NaHS,3H_2O$, and $2KHS,H_2O$, crystallise out. The anhydrous compounds are obtained by the action of sulphuretted hydrogen on solutions of sodium or potassium in ethyl alcohol, containing ethoxides. *E.g.*, $NaOC_2H_5 + H_2S = NaHS + C_2H_5{\cdot}OH$.

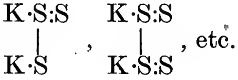
If to a solution of caustic potash or soda which has been saturated with sulphuretted hydrogen an equal volume of alkali is added, and the solution evaporated, the **monosulphides,** $K_2S,5H_2O$ and $Na_2S,9H_2O$, separate in colourless crystals.

By boiling alcoholic solutions of the hydrosulphides with sulphur, **potassium pentasulphide,** K_2S_5, and **sodium tetrasulphide,** Na_2S_4, are obtained. K_2S_5 forms bright orange-red crystals, giving a deep orange solution which becomes darker on heating. Na_2S_4 forms dark yellow crystals, giving a deep orange solution which also becomes darker on heating. **Sodium disulphide,** Na_2S_2, obtained by adding sodium to an alcoholic solution of Na_2S_4, forms bright yellow microscopic crystals, giving a deep yellow solution which does not darken on heating.

An examination of the freezing points of mixtures of the monosulphides and sulphur (*cf.* p. 768) showed that the following sulphides exist:

K_2S	K_2S_2	K_2S_3	K_2S_4	K_2S_5	K_2S_6
Na_2S	Na_2S_2	Na_2S_3	Na_2S_4	Na_2S_5	—

The constitution of these is probably:



$$\begin{array}{c}K{\cdot}S{:}S\\ |\\ K{\cdot}S\end{array}, \quad \begin{array}{c}K{\cdot}S{:}S\\ |\\ K{\cdot}S{:}S\end{array}, \text{ etc.}$$

LITHIUM, Li = 6·89.

Lithium.—Lithium is a rare but widely distributed element. It occurs in appreciable amounts only in a few rare minerals. Traces of lithium are found in milk, blood, plants, especially tobacco, and the soil. The **lithium minerals** are *triphylite*, $(Li,Na)_3PO_4 + (Fe,Mn)_3(PO_4)_2$ (1·6–3·7 per cent. Li); *petalite*, $LiAl(Si_2O_5)_2$ (2·7–3·7 per cent. Li); *lepidolite*, or *lithium mica*,

$(Li,K,Na)_2Al_2(SiO_3)_3(F,OH)_2$; and *spodumene*, $LiAl(SiO_3)_2$ (3·8–5·6 per cent. Li). Lithium also occurs in the waters of certain mineral springs, *e.g.*, in Baden, and at Redruth, in Cornwall; in radioactive minerals (*e.g.*, carnotite); and in the sea. Traces of lithium are found in most varieties of glass.

Lithium was discovered by Arfvedson (1817) in petalite and spodumene: the **metal** was isolated by Bunsen and Matthiessen in 1855, by the electrolysis of the fused chloride. Lithium may also be obtained by the electrolysis of a solution of lithium chloride in pyridine (C_5H_5N), and is a silver-white metal, harder than sodium, tarnishing in the air, although less readily than the other alkali-metals, and decomposing water, with evolution of hydrogen; it does not fuse on water like sodium and potassium, since its melting-point is higher (180°).

Lithium salts are extracted from the minerals, such as spodumene, in various ways. In one process the finely-powdered mineral is digested with concentrated sulphuric or hydrochloric acid, which is evaporated to render silica insoluble. The residue is taken up with water, and the solution filtered. To the filtrate the requisite amount of sodium carbonate is added to precipitate iron, alumina, magnesia, etc., and the filtrate is concentrated by evaporation. Excess of sodium carbonate is then added, when **lithium carbonate,** Li_2CO_3, is precipitated, as it differs from other alkali carbonates in being sparingly soluble in water. Another process is to fuse the mineral with barium chloride, extract with water, precipitate the filtrate with baryta-water, and evaporate. The residue contains sodium, potassium, and lithium chlorides, and is digested with a mixture of absolute alcohol and ether, in which **lithium chloride** alone is soluble. This salt (m.-pt. 606°) is one of the most deliquescent substances known.

Lithium burns, when heated in air above its melting point, with a white flame, forming the **monoxide** (*lithia*), Li_2O, a white substance which dissolves *slowly* in water, with only moderate rise of temperature, producing the **hydroxide**, LiOH. The latter is made by decomposing an aqueous solution of **lithium sulphate**, Li_2SO_4 (which, unlike the sulphates of the other alkali-metals, is soluble in alcohol), with baryta-water. It crystallises from the solution as $LiOH,H_2O$, and is a strong base. On heating the crystals in hydrogen at 140°, a white porous mass of the hydroxide, LiOH, remains, and at 780° the oxide, Li_2O, is formed. A **peroxide**, Li_2O_2, is formed by drying over P_2O_5 the precipitate, $Li_2O_2,H_2O_2,3H_2O$, obtained by adding hydrogen peroxide and alcohol to a solution of the hydroxide.

Lithium carbonate, Li_2CO_3, and **phosphate**, Li_3PO_4, are sparingly soluble, and are precipitated from lithium chloride solution by the corresponding sodium salts. The carbonate dissolves in a solution of carbon dioxide, forming a solution of **lithium bicarbonate**, $LiHCO_3$, which is more soluble than the normal carbonate (*cf.* $CaHCO_3$). The solution of the bicarbonate is called *lithia water.* On heating the normal carbonate it decomposes completely into the oxide and carbon dioxide. In these reactions, lithium shows a much closer resemblance to the metals of the alkaline-earths, *e.g.*, calcium, than to those of the alkalies.

Lithium salts, especially those of organic acids (citrate, salicylate) are used as a remedy for gout, since **lithium urate** is fairly soluble in water (1 part in 368 parts of H_2O at 20°). The **nitrate**, $LiNO_3$, is very deliquescent, and soluble in alcohol.

Lithium salts give a splendid crimson flame when moistened with hydrochloric acid and heated on a platinum wire in the Bunsen flame. The light emitted is resolved by the spectroscope into a very weak yellow line (6104 Å.), and a brilliant crimson line (6708 Å.). Lithium is separated from potassium by the solubility of its chloroplatinate, Li_2PtCl_6, and from sodium by the solubility of its chloride in a mixture of absolute alcohol and ether, and in pyridine, in all of which sodium chloride is insoluble. The **sulphate**, Li_2SO_4,H_2O, is readily soluble in water.

Lithium hydride, LiH, and **lithium nitride,** Li_3N, are formed by direct combination of the elements. The **carbide,** Li_2C_2, is formed in the electric furnace, and with water evolves pure acetylene: $Li_2C_2 + 2H_2O = 2LiOH + C_2H_2$.

Rubidium and Cæsium, Rb = 84·77, **and Cs** = 131·76.—**Rubidium** and **cæsium** occur in very small quantities in certain mineral waters (*e.g.*, Dürkheim, Ungemach, Bourbonne-les-Bains—1 litre of the latter contains 18·7 mgm. of RbCl and 32·5 mgm. of CsCl). Rubidium salts are absorbed from the soil by plants, but cæsium salts are not, and act as vegetable poisons. These two elements were the first to be discovered by the spectroscope (Bunsen, 1860). They give reddish-violet and blue flame colours, respectively (Latin *rubidus* = darkest red; and *cæsius* = the blue colour of the sky). They also occur in lepidolite, and some rare minerals. Carnallite (p. 791) contains about 0·035 per cent. of RbCl, which collects in the mother liquor from the preparation of potassium chloride.

These two elements may be separated from the other alkali-metals, and from each other, by utilising the different solubilities of the chloroplatinates and of the alums:—

Amounts in gm. of salts dissolved by 100 c.c. of water at 20°:—

	K.	Rb	Cs.
Alums	13·5	2·27	0·619
R_2PtCl_6	1·12	0·141	0·070

Cæsium carbonate is soluble in alcohol; rubidium carbonate is practically insoluble.

Rubidium salts are widely distributed, although in small amounts, but cæsium compounds are excessively rare. Although rubidium salts are absorbed by plants, they cannot replace potassium, and the plants die unless the latter is provided. Rubidium is feebly radioactive; its compounds emit β-rays. The higher halogen compounds of rubidium and cæsium have been mentioned (p. 771).

AMMONIUM (NH_4).

Ammonium compounds.—Ammonia, NH_3, readily combines with acids to form salt-like compounds. If a jar of hydrogen chloride is inverted over one of ammonia gas, dense white fumes are produced which settle on the sides of the jars as solid flakes of *salammoniac*, NH_4Cl.

Lavoisier regarded these compounds as containing ammonia and the acids; on this view, which was extended by Dumas in 1828, salammoniac would be *ammonia hydrochloride*, NH_3,HCl. Ampère (1818), however, supported the theory (first put forward by Davy in 1810) that these salts contain a radical **ammonium**, NH_4, which behaves as an alkali-metal. Salammoniac is therefore *ammonium chloride*, NH_4Cl, analogous to potassium chloride, KCl. This view of the constitution of the salts was favoured by Berzelius (1820).

The **ammonium theory** really had its origin in the discovery of what is called **ammonium amalgam**, obtained independently by Seebeck, in Jena, and by Berzelius and Pontin, in Stockholm (1808). If a solution of ammonium chloride is electrolysed with a mercury cathode (Fig. 153), the latter swells up in a curious manner, forming a soft, pasty mass, which rapidly decomposes, evolving hydrogen and ammonia in the ratio of 1 vol. to 2. This indicates that the decomposition: $N_2H_8 = H_2 + 2NH_3$ has occurred. Davy (1810) confirmed this observation, and showed that the "ammonium amalgam" could also be obtained by the action of potassium amalgam on a solution of ammonium chloride: $2K + 2NH_4Cl = 2KCl + N_2H_8$.

EXPT. 318.—Add a little sodium amalgam to a cold solution of ammonium chloride. Notice the way in which the amalgam swells up. Place a little of the ammonium amalgam in water: bubbles of hydrogen are evolved, and the liquid smells of ammonia.

Seely (1870) found by compressing ammonium amalgam in a tube under a piston that it obeyed Boyle's law, and concluded that it was simply a froth of hydrogen and ammonia gases in mercury. Pfeil and Lippman found that a similar amalgam was formed from salts of methylamine, *e.g.*, $N(CH_3)_4Cl$—methylammonium chloride, whereas aniline salts, containing *liquid* aniline, $C_6H_5NH_2$, did not react. The methylamine salts can give the *gaseous* free base, $N(CH_3)_3$. These experiments tell against the existence of free ammonium.

Other experiments speak in favour of the existence of ammonium in the amalgam. Although the latter does not reduce solutions of ferric chloride or copper sulphate at the ordinary temperature, it reduces solutions of copper, cadmium, zinc, and even barium, salts at 0°. The voltage required to deposit sodium on a mercury cathode is similar to that required in the formation of ammonium amalgam. An amalgam can be prepared by electrolysing a solution of tetramethylammonium chloride, a substituted ammonium salt, $N(CH_3)_4Cl$, in absolute alcohol at 0°, with a mercury cathode. This may contain $N(CH_3)_4$ or $N_2(CH_3)_8$; it reduces copper and zinc salts in alcoholic solution. The deep blue solutions obtained by dissolving sodium or potassium in liquid ammonia may be metal-ammoniums, NH_3Na and NH_3K, or $N_2H_6Na_2$ and $N_2H_6K_2$, or merely colloidal solutions of the metals; the latter can be filtered out under pressure.

Although there is no doubt as to the existence of the **ammonium ion**, $NH_4^{\bullet}$, in solutions of ammonium salts, there is not yet conclusive evidence that the electrically neutral ammonium radical, NH_4 or N_2H_8, can exist in the free state.

Ammonium chloride, NH_4Cl.—This compound, known as *salammoniac*, is prepared by neutralising ammonia solution with hydrochloric acid and evaporating. It is also made by boiling a solution of ammonium sulphate, which is the commonest ammonium salt (p. 552), with an equivalent amount of common salt: $(NH_4)_2SO_4 + 2NaCl \rightleftharpoons Na_2SO_4 + 2NH_4Cl$. The sodium sulphate separates, and is fished out: on cooling, ammonium chloride crystallises. It is purified by recrystallisation, on by sublimation. The latter operation is carried out by heating the salt in a cast iron basin provided with an iron dome, having a small hole at the top. The cake of ammonium chloride which sublimes into the dome is broken up, and forms tough, fibrous, irregular lumps, often stained in yellow patches with ferric chloride. A mixture of ammonium sulphate and common salt may also be heated in the same apparatus. An imitation of the sublimed product is made by strongly compressing the powdered salt: the well-known *voltoids*, used in batteries, are small tablets prepared by compression. Ammonium chloride is prepared in ammonia-soda works by crystallising the liquors from the bicarbonate filters, which contain NH_4Cl, NaCl, and $CaCl_2$, and drying the salt with hot air.

Ammonium chloride crystallises in feathery growths, consisting of aggregates of small octahedra or other forms of the regular system (p. 436), so that the crystals appear to belong to the hexagonal or tetragonal system. From a solution containing urea it crystallises in cubes isomorphous with NaCl and KCl.

The salt is readily soluble in water, and a considerable lowering of temperature results. It is very sparingly soluble in absolute alcohol. The aqueous solution is only slightly hydrolysed, and is neutral, but on boiling, ammonia escapes, leaving a distinctly acid liquid: $NH_4Cl + H_2O \rightleftharpoons NH_4{\cdot}OH + HCl \rightleftharpoons NH_3 + H_2O + HCl$. Ammonium chloride vapour is almost completely dissociated (p. 151): $NH_4Cl \rightleftharpoons NH_3 + HCl$, unless the salt has been carefully dried over P_2O_5, when it gives the normal vapour density corresponding with NH_4Cl. The ready dissociation of the salt on heating explains its action as a flux in soldering (p. 864): the oxides are converted into volatile chlorides by the hydrochloric acid, and a clean metal surface is left.

Ammonium fluoride, NH_4F, **bromide,** NH_4Br, and **iodide,** NH_4I, are obtained by neutralising the corresponding acids with ammonia. The salt NH_4F,HF, is also known.

Ammonium sulphides.—If ammonia gas and sulphuretted hydrogen are mixed in proper proportions and the mixture is cooled, **ammonium sulphide,** $(NH_4)_2S$, crystallises out. If equal volumes of the gases are mixed at the ordinary temperature, solid **ammonium hydrosulphide,** $NH_4{\cdot}HS$, is deposited. Both these compounds are colourless: they dissociate on heating into NH_3 and H_2S.

If sulphuretted hydrogen is passed through concentrated ammonia solution diluted with four times its volume of water, a solution of the hydrosulphide is formed. The normal sulphide does not appear to exist in solution. On cooling concentrated ammonia solution which has been treated with sulphuretted hydrogen, crystals of compounds of $NH_4{\cdot}HS$ and $(NH_4)_2S$ separate.

The freshly-prepared solution of the hydrosulphide is colourless, but oxidises rapidly on exposure to air and becomes yellow, owing to separation of sulphur, which dissolves in the excess of hydrosulphide to form yellow **polysulphides,** $(NH_4)_2S_x$. The same **yellow ammonium sulphide** is obtained by digesting flowers of sulphur with the solution of the hydrosulphide: the main product appears to be $(NH_4)_2S_4$. By distilling a dry mixture of salammoniac, quicklime, and sulphur, a blood-red liquid is obtained containing polysulphides of ammonium $(NH_4)_2S_x$. The composition of these, which may be similar to the potassium and sodium compounds (p. 795), has not been satisfactorily ascertained. On prolonged exposure to air, the solutions deposit sulphur, and form a colourless solution of ammonium thiosulphate, $(NH_4)_2S_2O_3$.

Ammonium sulphates, $(NH_4)HSO_4$ and $(NH_4)_2SO_4$.—The manufacture of **ammonium sulphate,** $(NH_4)_2SO_4$, from ammonia has been described (p. 552). Instead of using sulphuric acid as absorbent, a German patent specifies the absorption of ammonia in a suspension of calcium sulphate (gypsum), carbon dioxide being passed through the liquid. Calcium carbonate is precipitated, and a solution of ammonium sulphate is formed: $CaSO_4 + 2NH_3 + CO_2 + H_2O = (NH_4)_2SO_4 + CaCO_3$. Ammonium sulphate when pure forms large transparent crystals isomorphous with potassium sulphate (p. 512), and very soluble in water. On heating they decompose, partly with reduction to sulphur dioxide, nitrogen, and sulphur, and partly with evolution of ammonia, and formation of the **acid sulphate:** $(NH_4)_2SO_4 = NH_4{\cdot}HSO_4 + NH_3$. This may also be obtained in deliquescent crystals, by adding sulphuric acid to a solution of the normal sulphate, and crystallising. The **sulphite,** $(NH_4)_2SO_3$, is obtained in crystals by passing sulphur dioxide through ammonia.

Ammonium nitrate, NH_4NO_3.—This salt was first prepared by Glauber, and was called *nitrum flammans*. It is obtained by neutralising dilute nitric acid with ammonia or ammonium carbonate. On the large scale it is made by passing ammonia gas into 60 per cent. nitric acid; by the double decomposition of calcium nitrate and ammonium carbonate or sulphate; by the double decomposition of ammonium sulphate and sodium nitrate: $(NH_4)_2SO_4 + 2NaNO_3 \rightleftharpoons 2NH_4NO_3 + Na_2SO_4$; or by using sodium nitrate instead of common salt in the ammonia-soda process (p. 782): $NaNO_3 + NH_4{\cdot}HCO_3 \rightleftharpoons NH_4NO_3 + NaHCO_3$. A direct method of preparation has been described (p. 576).

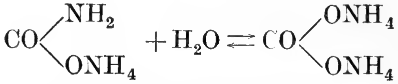
The salt exists in five crystalline forms, with definite **transition temperatures:** Tetragonal $\overset{-17^\circ}{\rightleftharpoons}$ (Rhombic)$_1$ $\overset{32{\cdot}1^\circ}{\rightleftharpoons}$ (Rhombic)$_2$ $\overset{84{\cdot}2^\circ}{\rightleftharpoons}$ Rhombohedral $\overset{125{\cdot}2^\circ}{\rightleftharpoons}$ Cubic $\overset{169{\cdot}6^\circ}{\rightleftharpoons}$ Liquid. The melting-point of the ordinary salt, containing a little moisture, is 165°. The transition at 84·2° is accompanied by an expansion, which may break a glass vessel in which the salt has solidified.

Ammonium nitrate is used in the preparation of nitrous oxide (p. 582), and is also a constituent of explosives. A mixture of 80 parts of ammonium nitrate and 20 parts of trinitrotoluene (*amatol*) was extensively used in the late war.

Ammonium nitrite is obtained as an explosive, deliquescent solid by passing the red fumes from nitric acid and arsenious oxide (p. 587) through lumps of solid ammonium carbonate in a cooled tube, dissolving in alcohol, and precipitating with ether. It is formed by mixing the red fumes with ammonia gas, as a white powder, although ammonium nitrate is also produced.

Ammonium carbonates.—The preparation of commercial ammonium carbonate, *sal volatile*, by the distillation of bones, horns, etc., was described by the later alchemists. The different materials were supposed at first to yield different kinds of volatile alkali; a particularly valuable variety from the medicinal point of view was obtained by distilling human skulls, especially of persons who had been hanged, although the dry distillation of vipers furnished a product which was also highly esteemed.

The salt is now obtained by a method described by Basil Valentine, viz., by subliming a mixture of 2 parts of chalk and 1 part of salammoniac, or ammonium sulphate, in iron retorts with lead receivers. The product is resublimed after the addition of a little water, and comes into the market as a white, semi-transparent, fibrous mass, covered on the outside with a white, opaque powder of the **bicarbonate,** $NH_4{\cdot}HCO_3$, and smelling strongly of ammonia. The commercial carbonate is a mixture of the bicarbonate and **ammonium carbamate,** $NH_4{\cdot}CO_2{\cdot}NH_2$. If the solid is treated with alcohol the carbamate is dissolved, leaving the bicarbonate; if it is exposed to air, the carbamate slowly volatilises; $NH_4{\cdot}CO_2{\cdot}NH_2 \rightleftharpoons 2NH_3 + CO_2$, leaving the bicarbonate as a white powder. The bicarbonate can be crystallised; at 60° it decomposes: $NH_4{\cdot}HCO_3 \rightleftharpoons NH_3 + CO_2 + H_2O$, although at the ordinary temperature it does not smell of ammonia. Commercial ammonium carbonate can be used as a baking powder since it volatilises completely on heating. If commercial ammonium carbonate is treated at 30° with concentrated ammonia solution, a **sesquicarbonate,** $2NH_4HCO_3,(NH_4)_2CO_3,H_2O$, is obtained in crystals. The **normal carbonate,** $(NH_4)_2CO_3$, is obtained by treating *sal volatile* with a small quantity of water, or by digesting it for two hours with concentrated aqueous ammonia at 12°, and drying the crystalline powder remaining, $(NH_4)_2CO_3,H_2O$, between filter-paper. It is formed when the carbamate is dissolved in water:



$$CO\begin{cases}NH_2\\ONH_4\end{cases} + H_2O \rightleftharpoons CO\begin{cases}ONH_4\\ONH_4\end{cases}$$

so that when the commercial carbonate is dissolved in ammonia solution the normal carbonate is formed. The **carbamate,** is deposited when 2 vols. of ammonia gas and 1 vol. of CO_2 are mixed: $2NH_3 + CO_2 \rightleftharpoons NH_4{\cdot}CO_2{\cdot}NH_2$.

EXERCISES ON CHAPTER XXXVIII

1. Give a brief account of the views previously held on the nature of the alkalies. How was Black able to demonstrate that the early views were incorrect? How were the alkali-metals isolated?

2. How do potassium and lithium occur in Nature? From what sources, and by what methods, are potassium salts prepared on the large scale?

3. How are sodium carbonate and caustic soda manufactured from common salt? What takes place when a solution of sodium carbonate is boiled with slaked lime?

4. How may sodium and potassium compounds be differentiated from each other in analysis? If you were given a mixture of sodium

chloride and potassium carbonate, how would you determine the amounts of each salt present ?

5. Give an account of the Ammonia Soda Process. How may it be modified so as to produce ammonium nitrate from Chile saltpetre ?

6. How are lithium salts prepared ? How do they differ from salts of sodium and potassium ?

7. Where do rubidium and cæsium salts occur ? How may these two elements be separated ?

8. Why are ammonium salts grouped with those of the alkali-metals ? What evidence is there of the existence of free ammonium ?

9. Describe the preparation and properties of: potassium iodide; ammonium carbonate; ammonium nitrate; sodium sulphides; potassium percarbonate.

10. Give a general account of the group of alkali-metals, paying particular attention to the gradation of the properties of the elements and their compounds with increase of atomic weight.

CHAPTER XXXIX

COPPER, SILVER, AND GOLD

General properties of the group.—The metals of this group, which occur in Nature in the free state, or else are very easily formed by the reduction of their compounds, were the earliest known elements. Although they occur in the same group as the alkali-metals, they differ considerably from the latter; the sole similarity is the existence of a series of compounds MX, in which the metals are univalent. This is the only type of combination known with silver, but copper forms a series of compounds in which it is bivalent, CuX_2, and gold a series in which it is tervalent, AuX_3, and both these are more stable, and better known, than the univalent series. Unlike the alkali-metals, copper, silver, and gold readily form **complex compounds,** in which the metal may be present either in the positive radical, *e.g.*, $[Cu(NH_3)_4]SO_4$, or in the negative radical, *e.g.*, $K[Ag(CN)_2]$.

Gold, having the highest atomic weight, differs in many respects from the other members of the group; this anomalous behaviour occurs frequently in the periodic system. Gold in many ways resembles platinum. Copper also shows a much closer relationship with mercury, which forms a unvailent and bivalent series of compounds (p. 870), than with silver or gold, although the cuprous salts resemble those of silver. Cuprous and silver chlorides are both white, insoluble substances, dissolving readily in ammonia. Although silver chloride is quite stable, cuprous chloride is readily oxidised to the cupric compound. The sulphides of copper and silver are isomorphous; the mineral *copper glance,* consisting chiefly of cuprous sulphide, Cu_2S, contains silver sulphide, Ag_2S, in isomorphous admixture in varying amounts.

The **heats of formation** of some compounds, in kgm. cals., are given below: the numbers for potassium are given for comparison:

R =		K.	Cu.	Ag.	Au.
R + Cl	...	104·3	32·85	29·4	5·8
R + Br	...	95·1	25·0	22·7	−0·1
R + I	...	80·1	16·25	13·8	−5·5
R_2 + O	...	164·6	40·8	5·9	?

These values correspond closely with the **affinities** of the various elements, since it has been shown by Nernst that in the case of *solid* compounds the heat of formation is an approximate measure of the affinity of the elements, although this does not usually hold for the formation of gaseous or dissolved substances.

COPPER. $Cu = 63{\cdot}07$.

Copper.—Copper occurs in the native, or metallic state, and was therefore used in very early times, especially in the form of its alloy bronze, which contains copper and tin. Working in bronze was practised at least as early as 2000 B.C.; the Bronze Age succeeded the Stone Age, and preceded that of Iron.

Copper was originally obtained by the Greeks and Romans from the island of Cyprus; the Latin name *aes cyprium* or Cyprian brass, afterwards became simply *cyprium*, and finally *cuprum*. These names were, however, with the Greek *chalkos*, also used for brass and bronze. The alchemists called the metal Venus (from its occurrence in Cyprus), and designated it by the symbol of the mirror, ♀. The precipitation of copper from the drainage-water of copper mines, by iron, was considered to be a case of transmutation until Van Helmont pointed out that the liquid originally contained a salt of copper, derived from copper pyrites in the mine. Boyle (1675) explained the reaction as one of simple displacement.

Native copper occurs in masses, and in veins traversing sandstone in Sweden, the Ural mountains, and in large quantities in the vicinity of Lake Superior. Cuprous oxide, Cu_2O, occurs as *cuprite* (or *red copper ore*); cupric oxide, CuO, occurs in smaller amounts as *tenorite*, or *melaconite*. Compounds of the carbonate and hydroxide occurring native, especially in the Ural districts, are *malachite*, $CuCO_3,Cu(OH)_2$, and *azurite* (or *chessylite*), $2CuCO_3,Cu(OH)_2$, which are bright green and deep blue in colour, respectively, and are used in works of art. In combination with sulphur alone, copper is widely distributed, although in relatively small amounts, in the forms of *chalcocite*, or *copper glance*, Cu_2S; and *covelline*, CuS, both probably formed by reduction of the sulphate by organic matter. The commonest ores are *copper pyrites*, or *chalcopyrite*, $CuFeS_2$, and *erubescite* (or *variegated copper ore*), Cu_3FeS_3, *i.e.*, sulphides of copper and iron. Considerable quantities of copper are extracted by the "wet process" from the residues left after burning iron pyrites containing copper (*cupreous pyrites*), in the manufacture of sulphuric acid (p. 778).

Copper occurs in the red colouring matter of the feathers of the toucan, and in the *hæmocyanin* of the blood of the cuttlefish, which acts like hæmoglobin (p. 697) as an oxygen carrier, but is blue in arterial and colourless in venous blood. Minute quantities occur in plants, especially in green peas.

Ordinary bread contains 4 mgm. of Cu per kgm., potatoes 2 mgm. As much as 100 mgm. of copper may be taken with food per day without danger, and higher organisms appear to have become to a certain extent immune to copper, although traces of lead and mercury are poisonous. Lower organisms, on the other hand, are very sensitive to copper salts. Traces of the latter are added to drinking water in America, to destroy bacilli and algæ, and a solution of copper sulphate mixed with chalk is used, under the name of *Bordeaux mixture*, for spraying potatoes, etc., to prevent the growth of blight. Seed-corn may also be steeped in a 0·5 per cent. solution of copper sulphate to prevent the development of smut.

The annual production of copper amounts to about 1,000,000 tons; about 650,000 tons were smelted in the United States in 1915.

Copper smelting.—Native copper is simply melted with a flux and then refined. Oxides (*e.g.*, cuprite) and carbonates (*e.g.*, malachite) are reduced by heating with carbon. Sulphide ores, from which a large amount of copper is obtained, are smelted by a somewhat complicated process, either in reverberatory furnaces (*Welsh process*), or in the blast furnace (*Mansfeld process*).

The Welsh process.—The simultaneous separation of the iron and sulphur from the ore is a matter of difficulty, since sulphur has a much greater affinity for copper than for iron. On roasting the ore, the iron is mainly oxidised to ferrosoferric oxide, Fe_3O_4, whilst the sulphur remains combined with the copper as cuprous sulphide, Cu_2S. This preliminary roasting is carried out in large flat furnaces, the ore being raked on the hearth by mechanical means so as to expose a large surface to the oxidising action of the air. The roasted ore is then fused at a high temperature in a **reverberatory furnace** with material containing silica. This combines with the oxide of iron to form a readily fusible silicate of iron, whilst the cuprous sulphide forms a lower layer, still containing some iron, called *coarse metal*. Fig. 387 shows the section of a reverberatory furnace used for copper smelting. The flames from the gas producer, *A*, strike against the arched roof of the furnace and are deflected on to the charge on the hearth, *E*. The secondary air for the combustion of the gas enters through the holes, *b*, *b*; that for the oxidation of the charge is admitted through the ports, *K*, *K*. The process is repeated, and nearly pure cuprous sulphide, called *white*, or *fine, metal*, is obtained. Blocks of fine metal are then roasted on the hearth of a reverberatory furnace, with a free supply of air. The sulphur is partly burnt off, with formation of cuprous oxide, Cu_2O. Reaction then takes place between the cuprous oxide and cuprous sulphide, with formation of metallic copper: $Cu_2S + 2Cu_2O = 6Cu + SO_2$. This roasting is carried out slowly; the blocks retain their shape, but become covered with blisters, due to escape of gas.

This *blister-copper* still contains 2 to 3 per cent. of impurities, mainly sulphur and iron. It is purified by melting a large quantity on a furnace hearth, skimming off the slag, and then removing the oxygen, dissolved in the metal in the form of cuprous oxide which would render the copper brittle, by covering the surface of the metal with powdered anthracite, and stirring with a pole of green birch-wood. Torrents of reducing gases bubble up through the metal, and the oxygen is removed. The metal is then tested by casting a small ingot, which is half cut through with a chisel and broken off. If the metal is sufficiently tough, the whole is cast in iron moulds. If the reduction has been carried too far, the metal becomes brittle, and is said to be *over-poled*. It is then exposed to the air for a short time to allow it to recover its tough pitch before casting. It will be seen from this description, which does not include all the actual operations, that the Welsh method of smelting copper is a complicated process. The effect of over-poling may be due to the reduction of oxides of other metals, which alloy with the copper and render it brittle.

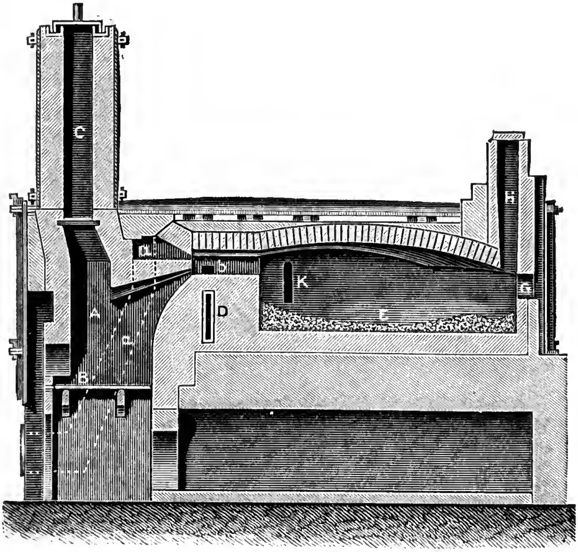


FIG. 387.—Reverberatory Furnace.

The Mansfeld process.—In this method the ore is smelted in **blast furnaces,** constructed of iron with a water cooling-jacket and lined in the lower portion with firebricks (Fig. 388). The roasted ore is mixed with coke or anthracite and a material containing silica, and charged into the top of the furnace. Air is forced in through pipes, *I*, *I*, and reactions occur leading to the formation of a slag and a *matte* corresponding with the coarse metal of the Welsh process. The slag and matte flow into the fore-hearth, *W*, the slag running away continuously from the opening, *M*, and the matte being tapped from the hole, *O*, as required. The matte is poured into a rectangular Bessemer **converter** (*cf.* p. 979), and a current of air is forced through it. The same reactions occur as in the former process and copper is produced. Sulphur is burnt off as sulphur dioxide, iron passes into the slag as silicate, and arsenic, etc., sublime.

Recent practice aims at smelting sulphide ores by the heat of combustion of the sulphur in them, with the addition of about 5 per cent. of fuel, in rectangular blast furnaces provided with a number of blowing pipes, or *tuyeres*. If a little boron is added to the fused copper it combines with the oxygen, nitrogen, and sulphur dioxide, and the cast metal is free from blow-holes, which would result from the escape of these gases on cooling. The boron is added in the form of an alloy with copper.

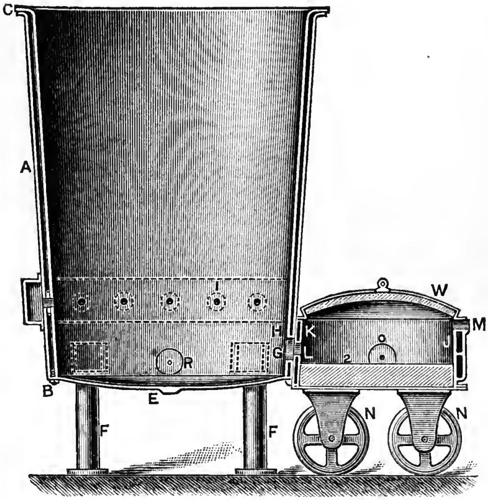


FIG. 388.—Blast Furnace for Manufacture of Copper.

Copper is also extracted by the **wet process.** The ore is leached with a solution of ferric sulphate, and a solution of copper sulphate is obtained. This is reduced by metallic iron. The burnt pyrites from the manufacture of sulphuric acid, if they contain copper, are worked up by roasting with 10–15 per cent. of salt in large shelf furnaces. The copper chloride, $CuCl_2$, formed is extracted with water, and any silver and gold present are precipitated as iodides. The copper is then reduced by scrap iron. In the **Rio Tinto process,** heaps of 100,000 tons of pyrites are exposed to air and rain. Slow oxidation occurs, and the copper sulphate formed is washed out with water. The remaining pyrites are exported for burning.

Copper refining.—Copper is largely used in the manufacture of wires and cables for carrying electric currents, and since its conductivity is appreciably lowered by traces of impurities, it is necessary to use a highly purified metal. The traces of silver and gold found in the crude metal are also of value. In refining copper, the **electrolytic process** is exclusively used; the large slabs of crude metal are immersed in a bath of copper sulphate solution acidified with sulphuric acid, and made the positive electrodes, or anodes in the bath. The cathodes consist of thin sheets of pure copper covered with a layer of graphite (Fig. 389). The copper dissolves from the anode as cupric ions, Cu$^{\cdot\cdot}$, and these travel to the cathode, where they give up their charges and are deposited as pure copper. Iron and zinc pass into solution as sulphates ; gold and silver (with some impurities) fall to the bottom as an *anode slime,* which is collected and cupelled (p. 819) for the purpose of obtaining the precious metals.

A similar process has been used since its invention by Jacobi in 1839, in **electrotyping**, *i.e.*, depositing copper electrolytically. This is used in reproducing statues and other works of art. The copper may be deposited on plaster casts covered with graphite to render them conducting, and the shell stripped off. In the same way, if an impression of printers' type is taken on gutta percha, and the latter covered with powdered graphite, a thin deposit of copper may be formed over the surface by electrolysis. This is stripped off, and backed by pouring on molten type-metal. The plate may then be used for printing. Copper may be deposited on iron by dipping the metal in a solution of copper cyanide in potassium cyanide, when a thin *adherent* film of copper is deposited (a spongy deposit is produced from copper sulphate) ; this is then thickened by electrolysis in a solution of copper sulphate. Iron rollers are in this way covered with copper for use in calico-printing.

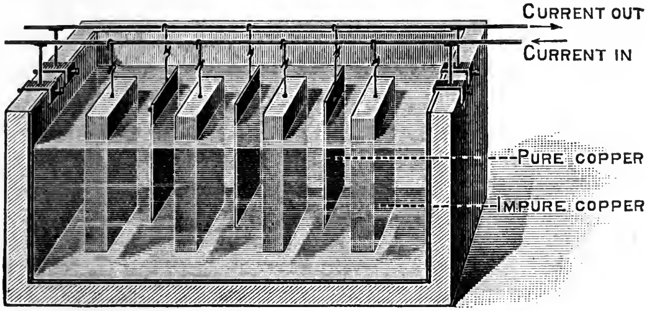


FIG. 389.—Purification of Copper by Electrolysis.

Copper is used for the driving-bands of steel projectiles. The driving-band consists of a copper band recessed into a groove in the base of the shell, and projecting slightly above the surface of the latter so as to be somewhat larger than the bore of the gun. On firing the shell, the copper is squeezed into the spiral rifling of the gun-barrel, and the gases are prevented from escaping, whilst the shell acquires a rotation which serves to keep it in its trajectory without turning over.

Alloys of copper.—The alloys of copper with other metals are of great technical importance. *Brass* (copper + zinc) and *bronze* (copper + tin) have been known from the earliest periods. They were made by heating copper with zinc and tin oxides, in presence of carbon. The tin or zinc oxide is reduced, and the metal alloys with the copper. These alloys are now made by fusing the copper, and adding the requisite amount of zinc or tin.

	Copper.	Tin.	Zinc.	Iron.	Phosphorus.
Common brass ...	2	—	1	—	—
Bronze (gun-metal) ...	9	1	—	—	—
Speculum metal ...	2	1	—	—	—
Bell metal	4–5	1	—	—	—
Phosphor-bronze ...	94·75–82·5	5–15	—	—	0·25–2·5
Delta metal	55	—	41	4	—
Dutch metal	80	—	20	—	—
Muntz metal	60	—	40	—	—
Old Roman coin ...	96·06	—	2·71	0·85	—
Modern bronze coin ...	95	4	1	—	—

Phosphor-bronze is hard, elastic, and tough; **delta metal** can be forged and rolled as well as cast, and is used for bearings, valves, and ships' propellers. **Muntz metal** is used as a sheathing for wooden ships. The definite compounds Cu_3Sn and Cu_4Sn are known.

Properties of copper.—A new surface of copper appears light red in colour, but this is due to the admixture of unchanged reflected light with that from which parts have been abstracted by reflection from the metal surface. The true colour of copper, produced by selective reflection, is a deep rose-colour, as is seen by looking at the fold of a piece of copper foil, cleaned with nitric acid, bent to a **V**-shape. The light is then reflected many times from the surface of the metal before entering the eye. The complementary colour, green, is seen in the light transmitted through thin leaves of the metal. Fused copper also emits a green light at high temperatures.

Pure copper is very malleable and ductile, and can be rolled into sheets, hammered into thin leaves, and drawn into wire. The metal may also be "spun" on the lathe, in the production of seamless vessels. Just below the melting-point copper becomes brittle, and appears to undergo allotropic change. Small quantities of impurities reduce the malleability of the metal.

Pure electrolytic copper has a density of 8·945; after hammering or rolling the density increases to 8·95. Pure copper powder is produced by allowing zinc to dissolve in a slightly acidified solution of copper sulphate, washing the precipitated copper with hot water and alcohol, and removing the small quantity of occluded hydrogen by heating in a vacuum.

The melting point of pure copper is 1083° ; the metal boils at 2310°, and can be distilled in a vacuum. The spongy and the fused metals occlude various gases ; when the metal solidifies these form bubbles, or give rise to " spitting " (p. 823).

On striking an arc under water between iron wires coated with copper, a colloidal solution is obtained, but this probably contains the oxide. By dialysing a solution of copper sulphate containing sodium hydroxide, and sodium lysalbate or protalbate, and then reducing, by warming with hydrazine, a dark red solution of **colloidal copper** is produced. If only partially reduced, a yellowish-red colloidal solution of cuprous oxide is obtained.

In the air, copper rapidly tarnishes, becoming covered with a very thin adherent brown film of oxide or sulphide, which causes the bright rose colour of the metal to deepen to brown. On prolonged exposure to moist air, a green film of basic carbonate (*verdigris*) is formed. On heating in air, the metal is readily oxidised, and the product forms scales which are black on the outside (**cupric oxide**, CuO), but are red on the side which was in contact with the metal (**cuprous oxide,** Cu_2O). If heated for a long time in air, cupric oxide is formed.

These two oxides correspond with the **cuprous** and **cupric salts**, in which copper is respectively univalent and bivalent. In solution, these salts form the **cuprous ion**, $Cu^{\cdot}$, and the **cupric ion** $Cu^{\cdot\cdot}$, respectively. The latter is blue ; the former (which readily decomposes into the cupric ion and metal : $2Cu^{\cdot} = Cu^{\cdot\cdot} + Cu$) is colourless.

CUPRIC COMPOUNDS, CuX_2.

Cupric oxide, CuO.—Cupric oxide, or *black oxide of copper*, is formed by the prolonged heating of the metal in air or oxygen, or by heating cupric nitrate. It is a black solid which is stable up to its melting point (about 1100°), but then evolves oxygen and leaves a solution of cuprous oxide, Cu_2O, in copper, which forms a solid solution on cooling. Cupric oxide is readily reduced by hydrogen, carbon, or organic substances, when heated below redness, and the metal remains. The oxide dissolves in the borax bead, colouring it green. If a little tin or stannous chloride is added to the bead, the cupric oxide is reduced to cuprous oxide, which forms an opaque red bead. In this way the green copper bead may be distinguished from that produced by ferrous compounds. Cupric oxide is used to give a green colour to glass.

When cupric oxide is dissolved in dilute acids, blue solutions of **cupric salts** are formed, *e.g.*, $CuO + H_2SO_4 = CuSO_4 + H_2O$. Concentrated hydrochloric acid gives a yellowish-green solution of cupric chloride, $CuCl_2$.

EXPT. 319.—Heat a spiral of copper gauze in a large Bunsen flame ;

a black layer of oxide is formed. Reheat the gauze and place it in a test-tube containing a few drops of methyl alcohol. The oxide is at once reduced to bright red copper.

Cupric sulphate, $CuSO_4$.—The commonest cupric salt is the **sulphate**, $CuSO_4$, commonly known simply as *copper sulphate*. This crystallises from water in large blue triclinic crystals, $CuSO_4,5H_2O$, called *blue vitriol*, or *bluestone*. It is obtained by dissolving cupric oxide in dilute sulphuric acid, or copper in hot concentrated sulphuric acid (p. 492): $Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$.

According to Cundall, the latter reaction leads first to the formation of **cuprous sulphate,** Cu_2SO_4; if the acid liquid is cooled and poured into water, a red precipitate of copper is formed: $Cu_2SO_4 = CuSO_4 + Cu$. **Cuprous sulphide,** Cu_2S, is also formed:

1. $8Cu + 4H_2SO_4 = 3Cu_2SO_4 + Cu_2S + 4H_2O$.
2. $2Cu + 2H_2SO_4 = Cu_2SO_4 + 2H_2O + SO_2$.

Secondary reactions then occur:

3. $5Cu_2SO_4 + 4H_2SO_4 = Cu_2S + 8CuSO_4 + 4H_2O$.
4. $Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + 2H_2O + SO_2$.
5. $CuS + 4H_2SO_4 = CuSO_4 + 4SO_2 + 4H_2O$.

Equations (1) and (3) give Pickering's equation:

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

Copper sulphate is prepared on the large scale by the action of dilute sulphuric acid on copper in the presence of air:

$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O,$$

or by the "weathering" of copper pyrites, which may first be roasted: $CuS + 2O_2 = CuSO_4$. Van Helmont (1644) obtained it by heating copper with sulphur, and exposing the moistened sulphide to air: he was thus able to prove that the salt contained copper. The preparation from copper and oil of vitriol was described by Glauber in 1648.

Commercial cupric sulphate usually contains ferrous sulphate, with one hydrated form of which, $FeSO_4,5H_2O$, it is isomorphous and forms mixed crystals. If the solution contains a considerable amount of copper, the crystals consist of $(Cu,Fe)SO_4,5H_2O$; if the iron predominates they have the composition $(Fe,Cu)SO_4,7H_2O$. Similar results are obtained with zinc sulphate. One salt may be said to "induce" the crystallisation of the other in a particular form. In order to purify the salt from iron, a concentrated solution of it is boiled with a little nitric acid. The iron is oxidised to ferric sulphate, which is not isomorphous with copper sulphate and is more soluble, hence it is left in solution on crystallisation, and pure cupric sulphate separates. A solution of the salt containing ferrous sulphate is used for steeping seeds to prevent "smut," and copper sulphate is employed in calico-printing, in the preparation of pigments (*e.g.*, *Scheele's green*, $CuHAsO_3$), and in electro-deposition. The salt is insoluble in alcohol; it is precipitated in small crystals, $CuSO_4,5H_2O$, when alcohol is added to the aqueous solution. Several crystalline hydrates of $CuSO_4$ are known (p. 204); on heating the blue pentahydrate crystals to 100° they crumble to a bluish-white powder of monohydrate, $CuSO_4,H_2O$. At 220–260°, this loses most of the combined water, but 0·04 per cent. is retained even at 360°, and the salt begins to lose sulphur trioxide at higher temperatures before all the water is expelled. The last molecule of water of crystallisation of a salt is often retained much more tenaciously than the others, and for that reason it was called *water of constitution* by Graham. The white powder obtained by dehydration at 260° is used in the detection of traces of moisture in alcohol, ether, etc., since it very readily absorbs water and becomes blue in colour. Anhydrous, or hydrated, copper sulphate readily absorbs hydrogen chloride, and is decomposed by the aqueous acid: $CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$. This reaction may be applied in separating hydrochloric acid from other gases, such as sulphur dioxide.

Cupric sulphide, CuS.—Cupric sulphide is a black solid formed by heating copper powder with excess of flowers of sulphur to a temperature below 440°, or by precipitating an acid solution of a cupric salt with sulphuretted hydrogen. In the moist state it is rapidly oxidised by air, forming a blue solution of the sulphate. It is slightly soluble in yellow ammonium sulphide, and a red compound, NH_4CuS_4, may be obtained from the solution. Cupric sulphide is less stable than cuprous sulphide, and loses sulphur when strongly heated alone, or in hydrogen: $2CuS = Cu_2S + S$.

Cupric nitrate, $Cu(NO_3)_2$.—Copper nitrate is prepared by dissolving the metal, oxide, or carbonate in dilute nitric acid, and on evaporation forms blue, deliquescent, prismatic crystals, $Cu(NO_3)_2,3H_2O$. At 24·5°, a hexahydrate separates. On heating, the salt loses water, and also nitric acid, forming a basic salt, $Cu(NO_3)_2,3Cu(OH)_2$. Copper nitrate possesses powerful oxidising properties: if a few crystals are moistened and wrapped in tinfoil, sparks are emitted. The anhydrous salt is obtained as a white powder by the action of a solution of nitrogen pentoxide in nitric acid on the crystalline hydrate.

Cupric halogen compounds.—**Cupric chloride,** $CuCl_2$, is obtained in the anhydrous form as a dark brown mass by burning copper in excess of chlorine, or by heating the hydrate, $CuCl_2,2H_2O$. It is formed as a yellow powder by adding concentrated sulphuric acid slowly to a concentrated solution of cupric chloride. When strongly heated, it loses chlorine and leaves cuprous chloride (p. 225). A crystalline hydrate, $CuCl_2,2H_2O$, is formed in emerald-green crystals by dissolving cupric oxide in concentrated hydrochloric acid and evaporating. In concentrated solutions it is yellowish-green; on adding concentrated hydrochloric acid the colour becomes yellow. This is due to the reversal of the ionisation: $CuCl_2 \rightleftarrows Cu^{\cdot\cdot} + 2Cl'$, the colour of the undissociated salt being yellow. A very dilute solution shows the pure blue colour of the cupric ion, $Cu^{\cdot\cdot}$; the green solutions probably contain a mixture of the blue ion and the yellow un-ionised salt. Cupric chloride is very deliquescent, and is also soluble in alcohol. The alcoholic solution burns with a fine green flame. A green flame is also formed by heating a little cupric oxide moistened with hydrochloric acid on a platinum wire in a Bunsen flame, or by heating the oxide in the flame and passing a little hydrochloric acid gas into the air-hole of the burner. Pure cupric oxide imparts no colour to the flame, but if moistened with chloroform, or an organic compound containing chlorine, a green flame results. This is used as a test for halogens in organic compounds.

An **oxychloride** of copper, $3CuO,CuCl_2,4H_2O$, is formed as a pale blue precipitate when caustic potash is added to an excess of cupric chloride solution. This compound occurs in Atacama, Peru, Bolivia, etc., in the form of a green sand called *atacamite*. It is being formed by the action of sea-water on copper pyrites on the south coast of Chile. The oxychloride is prepared for use as a pigment, called *Brunswick green*, by boiling copper sulphate solution with a small quantity of bleaching powder.

Cupric bromide, $CuBr_2$, is formed in black crystals by evaporating a solution of the oxide in hydrobromic acid in a vacuum desiccator over sulphuric acid. In solution, it shows the same colour changes as the chloride. Cupric iodide is not known (p. 817).

Cupric hydroxide.—If caustic potash or soda is added to a solution of a cupric salt, a pale blue gelatinous precipitate, usually regarded as the **hydroxide,** $Cu(OH)_2$, is formed, insoluble in excess of alkali. It appears, however, that the precipitate is, as was stated by Berthollet (p. 111), a basic sulphate, $CuSO_4,3Cu(OH)_2$. If a little of the copper solution is added to an excess of concentrated alkali, however, a deep blue colloidal solution of the hydroxide is formed. If the pale blue hydroxide is boiled with water, it becomes black, a hydrated oxide of the composition $4CuO,H_2O$, which is granular and easily filtered, being formed. On heating to redness, this is converted into the oxide, CuO.

Cupric carbonates.—Only **basic carbonates** of copper are known; the most important are the minerals *chessylite* (or *azurite*), $2CuCO_3,Cu(OH)_2$ (deep blue), and *malachite*, $CuCO_3,Cu(OH)_2$ (bright green). The green deposit (*verdigris*) formed on copper exposed to air has the same composition as malachite. If sodium carbonate solution is added to a solution of a cupric salt, carbon dioxide is evolved and a light blue precipitate of $CuCO_3,Na_2CO_3,3H_2O$ is formed : sodium bicarbonate precipitates $5CuO,3CO_2,Aq$.

Other cupric salts.—Cupric phosphate, $Cu_3(PO_4)_2,3H_2O$, is formed as a blue, crystalline powder by dissolving the basic carbonate in dilute phosphoric acid and heating to 70°. Basic phosphates occur as minerals. The **phosphide,** Cu_3P_2, is obtained as a black powder by boiling phosphorus with copper sulphate solution. When heated in hydrogen, it forms **cuprous phosphide,** Cu_3P. The black precipitate formed from copper salts and phosphoretted hydrogen is Cu_5P_2,H_2O. **Copper silicide,** Cu_2Si, is a grey compound obtained from the elements in the electric furnace. Copper containing 1–2 per cent. of silicon is hard, but has a good conductivity for electricity ; it is used for sliding contacts. Copper **orthosilicates,** CuH_2SiO_4, and CuH_2SiO_4,H_2O, occur as the minerals *dioptase,* and *chrysocolla,* respectively.

Copper peroxides, of the formulæ Cu_2O_3 and CuO_2,H_2O, are obtained as yellow powders by electrolysing concentrated caustic soda solution with a copper anode, and by allowing the hydroxide to stand in contact with hydrogen peroxide for several days, respectively. The compound CuO_2,H_2O is stable when dry.

CUPROUS COMPOUNDS, $\overset{I}{Cu}X$, or $(\overset{II}{Cu_2})X_2$.

Cuprous oxide, Cu_2O.—Red **cuprous oxide,** Cu_2O, is formed by the partial reduction of cupric compounds in the presence of alkalies.

EXPT. 320.—Dissolve 69 gm. of pure copper sulphate in 1 litre of water, adding 1 drop of sulphuric acid. Call this *Solution A.* Dissolve in another litre of water 350 gm. of Rochelle salt (sodium potassium tartrate, $NaKC_4H_4O_6,4H_2O$) and 100 gm. of caustic soda. Call this *Solution B.* Mix together 25 c.c. of *A* and 25 c.c. of *B* : the resulting deep blue liquid is called **Fehling's solution.** Boil this in a porcelain dish with a solution of glucose (grape sugar). A yellow precipitate of **cuprous oxide,** Cu_2O, is deposited, which quickly turns bright red. Filter, wash with boiling water, and alcohol, and dry in a steam-oven.

Cuprous oxide gives a red colour to the borax bead. When fused with glass it forms the cheaper kind of *ruby glass* (*cf.* p. 835). When treated with dilute sulphuric acid, a solution of *cupric* sulphate is formed, and metallic copper separates : $Cu_2O + H_2SO_4 = Cu_2SO_4 + H_2O \rightleftharpoons Cu + CuSO_4 + H_2O$. Dilute nitric acid dissolves the oxide with evolution of oxides of nitrogen, and a solution of *cupric* nitrate is formed. Concentrated hydrochloric acid dissolves cuprous oxide with formation of a colourless solution of *cuprous* chloride, Cu_2Cl_2, or a complex acid, H_2CuCl_3. The solution rapidly becomes green on exposure to air, owing to oxidation and formation of cupric chloride: $4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O$. The solution of cuprous chloride in hydrochloric acid is used in gas analysis for absorption of carbon monoxide. The solution in ammonia, which is colourless if metallic copper is present, is used to absorb acetylene.

Cuprous chloride, Cu_2Cl_2.—By heating copper with mercuric chloride, Boyle (1664) obtained **cuprous chloride,** Cu_2Cl_2, or CuCl, as a brown, resinous mass, turning green on exposure to air; he called it *resin of copper*. It is formed when copper burns in a limited supply of chlorine, or hydrochloric acid is passed over heated copper: $2Cu + 2HCl = Cu_2Cl_2 + H_2$. Copper does not dissolve in concentrated hydrochloric acid unless air is admitted, when *cupric* chloride is formed: $2Cu + 4HCl + O_2 = 2CuCl_2 + 2H_2O$. Cuprous chloride is most easily prepared by dissolving cuprous oxide in concentrated hydrochloric acid, or by reducing a solution of cupric chloride in concentrated hydrochloric acid, and pouring the solution into water. A white precipitate of cuprous chloride is thrown down.

The reduction of the cupric chloride may be effected by: (*a*) boiling with copper turnings until the solution becomes colourless: $CuCl_2 + Cu = Cu_2Cl_2$; (*b*) treating with zinc-dust: $2CuCl_2 + H_2 = Cu_2Cl_2 + 2HCl$; or (*c*) passing sulphur dioxide through the solution: $2CuCl_2 + H_2SO_3 + H_2O = Cu_2Cl_2 + H_2SO_4 + 2HCl$.

Expt. 321.—Dissolve 25 gm. of cupric oxide in 250 c.c. of concentrated hydrochloric acid in a flask. Add 50 gm. of copper turnings, and boil in a fume-cupboard until the solution is colourless. Pour the solution into a litre of previously boiled distilled water, filter off the cuprous chloride in a Büchner funnel, wash rapidly with boiling water, alcohol, and ether. Dry in a vacuum desiccator on a porous plate over sulphuric acid.

Cuprous chloride is a white powder which crystallises from concentrated hydrochloric acid in white tetrahedra. It melts at 434°, forming a brown, resinous mass on cooling. If exposed to light when moist it becomes dark coloured (*cf.* AgCl); in moist air it forms green cupric oxychloride, $CuCl_2,3CuO,4H_2O$. It dissolves readily in ammonia, forming a colourless solution of **cupro-ammonium chloride,** $Cu(NH_3)Cl,H_2O$, if all traces of oxygen are excluded. Crystals of this compound are obtained by boiling copper powder with a solution of ammonium chloride, and cooling. The colourless solutions in hydrochloric acid and ammonia readily absorb oxygen, becoming green and blue, respectively, and carbon monoxide, forming a solution of an unstable compound, $2CuCl,CO,H_2O$. Acetylene forms a bright red precipitate of **cuprous acetylide,** Cu_2C_2. This is explosive when dry; when warmed with hydrochloric acid, it evolves acetylene: $Cu_2C_2 + 2HCl = Cu_2Cl_2 + C_2H_2$.

Cuprous iodide, CuI, is precipitated as a white powder on addition of potassium iodide to a solution of cupric sulphate. Cupric iodide, if it is first produced, is at once decomposed into cuprous iodide and free iodine: $2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2$. If sulphur dioxide or ferrous sulphate is previously added, the formation of iodine is prevented:

$$2CuSO_4 + 2FeSO_4 + 2KI = 2CuI + Fe_2(SO_4)_3 + K_2SO_4.$$

If the iodine liberated in the first reaction is titrated with thiosulphate, the **volumetric estimation of copper** by this reaction is possible.

Cuprous sulphate, Cu_2SO_4.—This salt is formed to some extent when cupric sulphate solution stands in contact with copper: $Cu^{\cdot\cdot} + Cu \rightleftharpoons 2Cu^{\cdot}$, or $Cu_2^{\cdot\cdot}$. This is the cause of the inaccuracy of the ordinary copper coulometer. The pure salt is obtained as a white powder by heating cuprous oxide with dimethyl sulphate at 100°, washing with ether, and drying *in vacuo*. It is at once decomposed by water, with deposition of copper: $Cu_2SO_4 \rightleftharpoons CuSO_4 + Cu$. **Cuprous sulphite,** Cu_2SO_3,H_2O, is formed as a white precipitate on passing sulphur dioxide through a solution of cuprous acetate in acetic acid. **Cuprous sulphide,** Cu_2S, is a black, brittle mass formed when copper burns in sulphur vapour.

Expt. 322.—Place a few pieces of roll sulphur on the bottom of a small flask, and half fill the latter with copper turnings. Heat the flask: the copper glows with a red light, and a black mass of cuprous sulphide is formed. Moisten with water and expose to air; a blue solution of cupric sulphate is produced.

Cuprous cyanide, CuCN.—If potassium cyanide solution is added to a solution of cupric sulphate, the yellow cupric cyanide first precipitated rapidly decomposes with evolution of cyanogen, and white **cuprous cyanide** is formed. This dissolves in a solution of potassium cyanide, forming a colourless solution of **potassium cuprocyanide,** $KCu(CN)_2$, which is a salt of a complex anion, since it ionises as follows: $KCu(CN)_2 \rightleftharpoons K^{\cdot} + Cu(CN)_2'$. Only traces of copper ions from the further ionisation: $Cu(CN)_2' \rightleftharpoons Cu^{\cdot} + 2CN'$, are formed, and the solution is not precipitated by sulphuretted hydrogen, since the concentration of copper ions is not sufficient to exceed the solubility product of the very sparingly soluble cuprous sulphide.

Potassium thiocyanate gives with a solution of cupric sulphate to which ferrous sulphate or sulphur dioxide has been added a white precipitate of **cuprous thiocyanate,** CuCNS.

Other cuprous compounds.—**Cuprous hydride,** CuH, is a very unstable yellow precipitate obtained by reducing a solution of copper sulphate with a hypophosphite at 70°. It evolves hydrogen with hydrochloric acid: $CuH + HCl = H_2 + CuCl$. **Cuprous nitride,** Cu_3N, is a dark green powder formed by heating cuprous oxide in ammonia gas.

If copper sulphate solution is added to a solution of sodium stannite, obtained by adding an excess of caustic soda solution to stannous chloride, an olive-green precipitate of **copper suboxide,** Cu_4O, is thrown down. If this is added to dilute sulphuric acid, a colourless solution is formed. This, after a few seconds, becomes deep purple in colour, and deposits red metallic copper.

Cuprammonium compounds.—Cupric hydroxide readily dissolves in ammonia (which precipitates it from a cupric salt), forming a deep blue solution, known as **Schweitzer's reagent.** This dissolves cellulose (filter-paper, cotton-wool), and if the solution is then squirted into dilute acid, a thread of amorphous cellulose is formed, which is one variety of **artificial silk.** The solution may also be applied to canvas to form a water-tight coating of amorphous cellulose (*Willesden canvas*): some method of preserving cellulose by impregnation with copper was known to the ancient Egyptians. The blue ammoniacal solution appears to contain the complex **cuprammonium cation,** $Cu(NH_3)_4^{\cdot\cdot}$; if a solution of cupric sulphate is precipitated with ammonia, and the precipitate dissolved in excess of ammonia, a deep blue solution is formed. If a layer of alcohol is poured carefully over this solution in a cylinder, the latter corked to prevent evaporation, and the whole allowed to stand, long, transparent, deep blue rhombic prisms of **cuprammonium sulphate,** $Cu(NH_3)_4SO_4,H_2O$, are deposited. This salt may be regarded as $CuSO_4,5H_2O$, in which 4 of the molecules of water of crystallisation are replaced by molecules of ammonia. Cupric chloride forms **cuprammonium chloride,** $Cu(NH_3)_4Cl_2,2H_2O$, which crystallises on cooling a hot solution of cupric chloride saturated with ammonia gas. Anhydrous cupric chloride absorbs ammonia gas, forming the compound $CuCl_2,6NH_3$, which readily dissociates on heating, forming $CuCl_2,4NH_3$ and $CuCl_2,2NH_3$.

SILVER. $Ag = 107{\cdot}04$.

Silver.—Silver has been known from the earliest times; its association with the moon led to the name Luna, or Diana, given to it by the alchemists, who represented it by the symbol of the crescent moon, ☾. It is not oxidised by pure air or oxygen, either in the cold or when heated, and is an example of a **noble metal** (silver, gold, platinum). In ordinary air it slowly tarnishes, and becomes covered with a thin adherent film, which exhibits the colours yellow, blue, and black, with increasing thickness. This film is composed of **silver sulphide,** Ag_2S, formed by the decomposition of hydrogen sulphide present in the air: $H_2S + 2Ag = Ag_2S + H_2$.

The staining of silver spoons used with eggs is also due to the formation of silver sulphide from the combined sulphur in the albumin of the egg. The tarnish is readily removed by a dilute solution of potassium cyanide, followed by washing in plenty of water.

Silver occurs frequently in the **native** state, often in large masses, in Norway, Peru, and Idaho, occasionally nearly pure, but usually containing copper and gold. Important **ores of silver** are the sulphide, *argentite* (or *silver glance*), Ag_2S (the commonest ore); *chlorargyrite* (or *horn-silver*), AgCl; *pyrargyrite* (or *ruby-silver*), Ag_3SbS_3; *stromeyerite* (or *silver-copper glance*), $(Cu,Ag)_2S$; *stephanite*, Ag_5SbS_4. Less important are *proustite*, Ag_3AsS_3, the bromide, AgBr, and the iodide, AgI. Traces of silver occur in sea-water (Proust, 1787).

Metallurgy of silver.—Silver is extracted from its ores by several processes, the most important being:

(1) alloying with lead, and removing the lead by oxidation **(cupellation)**;
(2) alloying with lead, followed by the separation of silver from the argentiferous lead by dissolving it in fused zinc (**Parkes process**);
(3) amalgamation with mercury, and separation of the mercury from the silver by distillation;
(4) dissolving out the silver salts from the ore by a solution of common salt, sodium thiosulphate, or potassium cyanide, followed by precipitation (**wet processes**).

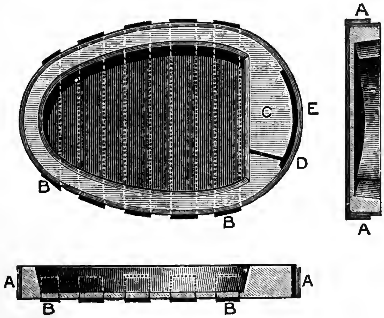


FIG. 390.—Cupel.

The **cupellation process** is the most ancient. In it, the silver ore is smelted with a lead ore, and the resulting alloy of silver and lead is treated to separate the silver. The lead obtained from **galena** is nearly always argentiferous, and forms an important source of silver. Formerly the alloy was treated directly by melting it on a flat dish formed of bone ash (Fig. 390). called a **cupel**, and a blast of air driven over the surface of the metal (Fig. 391). The lead is oxidised to lead monoxide, or litharge, PbO, which fuses and is swept away by a blast of air. The last portions of litharge are absorbed by the porous cupel, and a bright button of silver is left. In the last stage of the process the litharge film becomes so thin that iridescent colours are seen; the bright silver surface then "flashes" out. In Germany, the furnace-hearth is formed of marl, and the cupellation is performed in one operation instead of the alloy being added in successive quantities, as in the English process. Alloys containing considerable amounts of lead, such as the argentiferous lead from galena, are treated to effect a partial separation before cupellation. This is carried out in two ways, known as the Pattinson process and the Parkes process.

The Pattinson process (1833).—If fused argentiferous lead is cooled, a point is reached when pure lead separates out in crystals. This will occur at a temperature below the freezing point of pure lead, because of the depression of freezing point by the dissolved silver (p. 766). The crystals of lead are withdrawn by perforated iron ladles, and the remaining liquid alloy becomes increasingly rich in silver until, if the process were carried far enough, lead and silver would begin to separate out together at the eutectic point. In practice, seven-eighths of the original lead is removed. The process is carried out in a row of iron pots, the lead separated being passed on from pot to pot to be remelted, and the liquid alloy passed in the other direction. The silver gradually accumulates in the alloy at one end of the series, and desilvered lead at the other. The rich alloy is then cupelled. In the modification known as the **Luce-Rozan process,** only two pots are used, an upper or melting pot, and a lower or crystallising pot, holding 7 and 21 tons respectively. The lead is deposited in the latter by blowing steam at 50 lb. pressure through the fused metal, whilst cold water is sprayed on the surface. When two-thirds of the lead has separated, the liquid is strained off through a perforated plate. The separated lead is remelted and the process repeated until the proportion of silver retained mechanically in the lead crystals is sufficiently small.

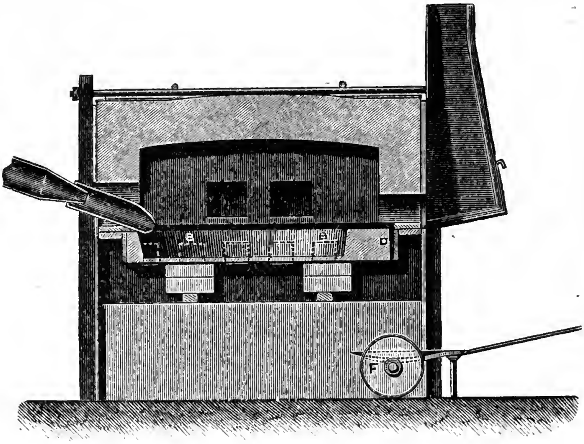


FIG. 391.—Cupellation Furnace.

The Parkes process (1850).—Molten lead can dissolve only 1·6 per cent. of zinc, and molten zinc can take up only 1·2 per cent. of lead. Silver, however, is soluble in zinc. If, therefore, zinc is added to molten lead containing silver, the molten alloy of zinc and silver floats to the surface, and solidifies on cooling. It is skimmed off with a perforated ladle, and strongly heated with carbon in a fireclay retort. Zinc distils off, leaving silver, which is cupelled. The zinc alloy may also be electrolysed (as anode) in zinc chloride solution; zinc is deposited on the cathode, and silver is left. To remove traces of zinc dissolved in the lead, the latter is heated to redness and a blast of steam forced through it, when zinc oxide rises to the surface, leaving the lead. For a ton of lead containing 14 oz. of silver, only 22·4 lb. of zinc are required. This process is superseding the Pattinson method.

Any gold present is also removed by the zinc. The desilvered lead contains only 0·0004 per cent. of silver, whilst that obtained by the Pattinson process contains 0·001–0·002 per cent.

Amalgamation and wet processes.—The **amalgamation process** has been used in Mexico, where fuel is scarce; it was invented by Bartolomeo de Medina in 1557. The ores, containing metallic silver, silver chloride and sulphide, and a large quantity of rock, are finely crushed in stamping mills worked by mules, and the fine mud is mixed with a little salt. The mass is then well trodden by mules on a paved floor, or *patio*. Mercury is then added, together with a little roasted pyrites, containing cupric and ferric sulphates, and the treading is continued for fifteen to forty-five days. Copper chlorides are probably first produced from the roasted pyrites and salt, and these decompose the silver sulphide with formation of the chloride: $CuCl_2 + Ag_2S = 2AgCl + CuS$; or $2CuCl + Ag_2S = Cu_2S + 2AgCl$. The silver chloride then dissolves in the brine, and is reduced by the finely-divided mercury: $AgCl + Hg = Ag + HgCl$. The silver forms an amalgam with the excess of mercury. (About 1 per cent. of sodium is now added to the mercury, to prevent the latter forming a fine powder, which would be lost in washing.) The amalgam is separated by washing, the calomel being lost, the excess of mercury is pressed out from the amalgam in canvas bags, and the residue distilled in iron retorts to recover the mercury. This process has, since **1904**, been gradually replaced by the cyanide process (see below).

In the **wet processes** the ore is roasted, either alone, when soluble silver sulphate is formed and can be lixiviated, or with salt, when silver chloride is produced, which is extracted with salt solution, or a solution of sodium thiosulphate. From these solutions, the silver is precipitated by sodium sulphide as silver sulphide. In the modern **cyanide process,** the unroasted ore, finely ground in ball mills, is leached with a 0·7 per cent. solution of sodium cyanide, the slime being well agitated by a stream of air. Soluble **sodium argento-cyanide,** $NaAg(CN)_2$, is formed, the sodium sulphide also produced, which would tend to stop the reaction, being oxidised to thiosulphate and sulphur by the current of air : $Ag_2S + 4NaCN \rightleftharpoons 2NaAg(CN)_2 + Na_2S$. The silver is precipitated from the solution by scrap zinc.

Refining of silver.—Silver is **refined** by cupellation, or by the **Moebius electrolytic process** (1884). The electrolyte consists of silver nitrate solution with about 1 per cent. of free nitric acid ; the cathode is a plate of pure silver and the anode a block of the silver to be refined. Silver is deposited, copper dissolves, and the gold present in the anode alloy deposits as a slime. The copper must not accumulate in the solution beyond 4–5 per cent. The gold slime is collected in a canvas bag round the anode.

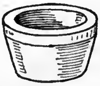


FIG. 392.—Cupel.

Silver alloys.—Commercial silver is alloyed with copper, because the pure metal is too soft for coinage or jewelry work. The proportion of silver in 1,000 parts of alloy is called the *fineness*. British silver coin since the time of Edward I. has had a fineness of 950 ; in France, Germany, and Austria the silver coinage has a fineness of 900. The metal still retains the pure white colour of silver.

The composition of the alloy used by the Mint is ascertained yearly in a public trial, known as the *trial of the pyx*, conducted by competent assayers appointed by the Goldsmiths' Company, who also carry out trials with gold coin. The **assay** is made by heating a weighed portion of the alloy with a little pure lead on a bone-ash **cupel** (Fig. 392) in a **muffle furnace** (Fig. 393). This is a furnace in which a fireclay oven containing the cupels is strongly heated on the outside, the mouth of the muffle being only loosely closed, so as to admit air. The copper is oxidised, and the oxide dissolves in the lead oxide, which is easily fusible, and is absorbed by the cupel. The trial of the cupel is described by the Latin Geber.

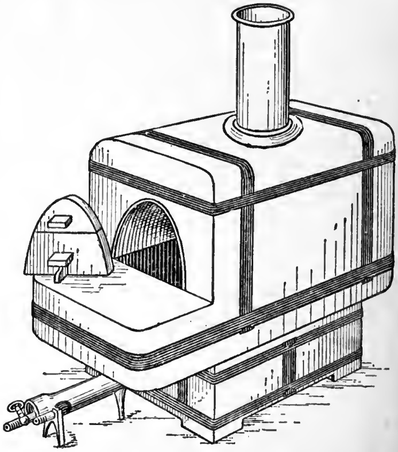


FIG. 393.—Muffle Furnace for Cupellation.

Silver goods are often treated by heating in air ; the copper in the alloy oxidises ; the oxide is removed by dilute acid, leaving a surface of pure silver. Test-portions must therefore be taken from the mass of the metal.

Pure silver.—In order to obtain pure silver from its alloy with copper, the latter is dissolved in dilute nitric acid, when copper nitrate, $Cu(NO_3)_2$, and **silver nitrate,** $AgNO_3$, are formed. The solution is evaporated to drive off some of the excess of acid, and diluted with water. Hydrochloric acid is added in slight excess. A curdy white precipitate of **silver chloride,** AgCl, is produced. This is filtered off and washed with hot water till free from acid. To obtain silver from the chloride it is treated in one of several ways.

(*a*) The chloride is fused in a crucible with sodium carbonate, when a button of pure silver is formed : $4AgCl + 2Na_2CO_3 = 4Ag + 4NaCl + 2CO_2 + O_2$.

(*b*) The silver chloride is boiled with a solution of caustic potash and grape-sugar : the oxide is first formed as a dark-brown powder, which is then converted into a grey powder of metallic silver, together with a dark-brown solution containing the oxidation products of the sugar : $2AgCl + 2NaOH = Ag_2O + 2NaCl + H_2O$; $Ag_2O = 2Ag + O$. The silver is then well washed with boiling distilled water.

(*c*) Dilute sulphuric acid is poured over the silver chloride, and a stick of pure zinc placed in the mixture. The chloride is reduced by the nascent hydrogen, forming a grey mass of silver powder, which is washed and dried on a water-bath : $AgCl + H = Ag + HCl$. The silver from (*b*) or (*c*) may be fused in a crucible with sodium carbonate to form a button. (If silver is fused in a glazed porcelain crucible, the latter becomes yellow, owing to the formation of silver silicate.) Stas distilled silver in a lime crucible with the oxy-hydrogen blowpipe. Richards (1905) showed that Stas's silver probably contained a little occluded oxygen, which may be removed by heating in a vacuous tube at 400°.

Fused silver dissolves oxygen, which is liberated as soon as the metal begins to solidify. Ten gm. of silver at 1020° dissolve 20·5 c.c. of oxygen (at S.T.P.). The solid crust is violently disturbed, and the metal "spits." This phenomenon, which is easily observed with the metal fused on a cupel, is shown only by pure silver, and is a good test of the completion of cupellation.

Properties of silver.—Silver melts at 962° in the absence of air, and at 956° in air. It boils at 1955°, forming a blue vapour, the density of which corresponds with the formula Ag. The density of the solid is 10·5 ; it contracts on fusion, like ice, and the solid floats on the molten metal. Silver is very malleable and ductile ;

it can be beaten into leaves 0·00025 mm. thick, which become somewhat transparent on heating. Very thin films deposited on glass (*cf.* below) also transmit blue light.

Silver is attacked by boiling concentrated sulphuric acid, or cold dilute nitric acid, but resists the action of alkalies, even when the latter are fused. Silver crucibles are therefore used in the laboratory for fusion with caustic alkalies, but may be replaced by those of pure nickel, although the latter is slightly attacked.

Silver deposited on glass by reduction is used in the manufacture of **mirrors.**

EXPT. 323.—Clean a test-tube with boiling nitric acid, wash well with water, and prepare in it a solution of silver nitrate. Add *dilute* ammonia drop by drop until the precipitate of silver hydroxide is *almost* redissolved. Then add caustic potash and a solution of Rochelle salt (potassium sodium tartrate—this acts as the reducing agent). Place the tube in a beaker of water and heat the latter to boiling. A mirror of silver is deposited on the tube.

Colloidal silver.—A colloidal solution of silver may be prepared by **Bredig's method** of striking an electric arc between silver wires under water. The metal is volatilised, and condensed in the water in the form of very small particles, which remain in colloidal suspension. Colloidal solutions are also formed by reduction.

EXPT. 324.—To 200 c.c. of a 10 per cent. solution of silver nitrate add quickly a solution formed by mixing 200 c.c. of a 30 per cent. solution of ferrous sulphate and 200 c.c. of a 40 per cent. solution of sodium citrate, the mixture being carefully neutralised with soda before addition to the silver solution. A lilac precipitate of silver is formed, which is filtered off. and washed with a 5–10 per cent. solution of ammonium nitrate. It is then soluble in pure water, forming a red, transparent solution. If silver nitrate, ferrous sulphate, or magnesium sulphate is added to the red solution the colloidal silver is coagulated, and is then no longer soluble in water, whereas silver thrown down from the solution by ammonium nitrate redissolves on washing. The former salts are **adsorbed** by the silver precipitate. If the precipitates are dried, they form blue solids.

Carey Lea (1889) considered these substances to be allotropic modifications of silver; it is now recognised that they are ordinary silver in the **colloidal** condition (see *colloidal gold*, p. 834). By heating silver nitrate with an alkaline solution of sodium protalbate or lysalbate, Paal (1902) prepared a yellow solution of colloidal silver. If this is dialysed, and evaporated on a water-bath, a brownish-black powder, containing as much as 93 per cent. of silver, and soluble in water, is formed. This is called **collargol.**

The colloidal modifications of silver do not conduct electricity; on heating, they all give ordinary silver. Traces of the substances present in solution are always adsorbed by the colloid, which does not seem to exist in a perfectly pure state.

Electroplating with silver.—The electro-deposition of silver takes place in a very direct manner, free from secondary reactions, and is applied in the **silver coulometer** for the measurement of current strength. The **International ampere** is defined in terms of such an instrument (p. 282), as the current which deposits 0·001118 gm. of silver per second from a specified silver solution.

The apparatus in ordinary use (Fig. 394) for measurement of currents consists of a platinum dish or crucible, which is carefully weighed, and contains a solution of silver nitrate (300 gm. per litre). The dish is placed on a brass plate on the base of the stand, which is connected with the negative terminal. The anode is a rod of pure silver, suspended by a clamp in the solution. A small glass cup is suspended under the anode, to retain detached pieces of the latter. The crystalline deposit of silver adheres to the dish; it is washed with water and alcohol, the dish dried in an air-oven, and weighed. If the experiment lasts for t seconds, and m mgm. of silver are deposited, the *mean* current strength is $m/(t \times 0{\cdot}001118)$ ampere.

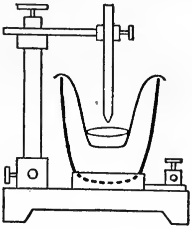


Fig. 394.—Silver Coulometer.

Copper articles are **electroplated** with silver by cleaning their surfaces and suspending them in a solution of silver cyanide in excess of potassium cyanide, the anode being a plate of pure silver. The solution contains the complex compound **potassium argentocyanide,** $KAg(CN)_2$, which ionises in a similar manner to the copper compound: $KAg(CN)_2 \rightleftharpoons K^{\cdot} + Ag(CN)_2'$. The anion is very slightly dissociated: $Ag(CN)_2' \rightleftharpoons Ag^{\cdot} + 2CN'$, and the silver ions are deposited on the cathode as a coherent film of metal instead of the crystalline metal, which is formed from silver nitrate solution. The dissociation of the complex ion proceeds as silver ions are withdrawn from the solution. The cyanide ions are discharged on the silver anode, forming silver cyanide, which dissolves in the solution. The net result is the transfer of silver from the anode to the cathode.

This process was invented by Wright, of Birmingham, in 1840, and a patent was taken out by the firm of Elkington, which still produces electroplated goods. Previous to the use of electro-plating, copper goods were plated with silver by laying a strip of silver on a bar of clean copper, heating, and rolling the bar to the required thickness. This is known as **Sheffield plate,** and the layer of silver is much thicker than in the case of electro-plated goods.

Compounds of silver.—Unlike copper and gold, silver forms only one series of compounds, in which the element is univalent. It does not form basic salts, a tendency which is prominent in the case of copper. The silver salts are largely ionised in solution, the **silver ion,** $Ag^{\cdot}$, being split off. Salts of gold do not ionise in this simple way. The test for the silver ion is the formation of a white curdy precipitate of **silver chloride,** $AgCl$, when a solution of a chloride is added. This precipitate is insoluble in dilute nitric acid, but is readily soluble in ammonia, potassium cyanide, or sodium thiosulphate. In all cases complex compounds, which give only a few silver ions in solution, are formed when the silver chloride dissolves. The concentration of silver ions is not sufficient to exceed the solubility product of silver chloride.

Silver nitrate, $AgNO_3$.—The most important salt of silver is the **nitrate,** $AgNO_3$, the preparation of which is described by the Latin Geber: "Dissolve silver in aqua fortis (*aqua dissolutiva*); boil in a phial with a long neck, not stopped, until one-third has been consumed (evaporated), and finally set in a cold place. You obtain small fusible stones, transparent as crystal." The salt forms large transparent rhombic plates, melting at 209°. The fused salt may be cast into sticks, and is then used as a cautery under the name of *lunar caustic.* The alchemists also called it *lapis infernalis.* It is readily decomposed by organic matter, such as paper, cork, or the skin, metallic silver being deposited. The silver is deep black in colour, so that a solution of silver nitrate is used as an indelible ink for marking linen. The same black stain is formed on the skin; it can be removed from the articles by a dilute solution of potassium cyanide. Silver nitrate is poisonous, but is given internally in small doses in nervous diseases. The salt is soluble in alcohol.

Silver nitrate decomposes when strongly heated; oxygen and nitrogen dioxide are evolved, and silver remains. The decomposition point is much higher than that of copper nitrate, so that copper nitrate may be separated from silver nitrate by heating, adding water, and filtering from the copper oxide. Copper may also be separated by adding a little caustic soda to a portion of the solution, filtering off and washing the silver oxide, Ag_2O, and boiling it with the rest of the solution. Copper oxide is precipitated, and the silver oxide goes into solution as nitrate.

Solid silver nitrate absorbs ammonia gas, with evolution of heat, and formation of a compound $AgNO_3,3NH_3$. If ammonia is added to a solution of the nitrate until the oxide first precipitated is dissolved, and the liquid evaporated, crystals of a compound $AgNO_3,2NH_3$ separate. This is the nitrate of a complex cation, $Ag(NH_3)_2{}^{\cdot}$. Double salts, *e.g.*, $AgNO_3,2NaNO_3$ and $AgNO_3,KNO_3$, are known.

Silver nitrite, $AgNO_2$, is formed as a crystalline precipitate when solutions of silver nitrate and potassium nitrite are mixed. It decomposes on heating, evolving oxides of nitrogen.

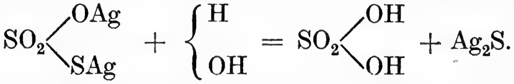
Silver oxide, Ag_2O.—Finely-divided silver, when heated to 300° in oxygen under pressure, forms a brown **oxide,** Ag_2O. If caustic soda is added to a solution of silver nitrate, a brown precipitate of silver oxide, Ag_2O, is thrown down. This may be dried at 60–80°, and is then black. The **hydroxide,** AgOH, is said to be precipitated from alcoholic silver nitrate by alcoholic potash at $-30°$. The oxide may also be prepared by boiling the chloride with caustic soda solution. It is very slightly soluble in water ($3 \cdot 10^{-7}$ gm. mol. per litre), forming a solution alkaline to litmus, and the moist solid readily attracts carbon dioxide from the air, producing **silver carbonate,** Ag_2CO_3. The latter is precipitated as a light yellow powder when a carbonate is added to a solution of silver nitrate. With excess of potassium carbonate, a double carbonate, $KAgCO_3$, is formed as a white precipitate.

Silver oxide gives off oxygen at 300°. It is used as an oxidising agent in organic chemistry, and for giving a yellow colour to glass, a yellow silicate, Ag_2SiO_3, being formed. When the oxide is dissolved in ammonia, and the solution exposed to the air, a black precipitate of the nitride, Ag_3N, is deposited. This is very explosive when dry, and is called **fulminating silver.**

A **peroxide,** Ag_2O_4, is deposited, mixed with silver nitrate, on the anode in the electrolysis of silver nitrate with platinum electrodes. It evolves oxygen on heating.

Halogen compounds of silver.—Silver fluoride, AgF, is the only halogen compound of silver appreciably soluble in water. Hydrofluoric acid does not act on the metal, but dissolves the oxide. On evaporation in a vacuum, crystals of AgF,H_2O are deposited, which cannot be completely freed from water by heating. By evaporating the solution in the air, very deliquescent crystals of $AgF,2H_2O$ are formed. The fused salt, which contains metallic silver ($4AgF + 2H_2O = 4Ag + 4HF + O_2$), is an *elastic* black mass, easily cut with scissors. Silver fluoride, under the name of *tachyol*, has been proposed for sterilising water.

Silver chloride, AgCl, occurs native as *horn-silver*, described by Conrad Gesner (1565) as *argentum cornu*, and by Matthesius (1585) as "glass-ore, transparent like horn in a lantern." It is readily prepared as a curdy white precipitate by adding hydrochloric acid, or a chloride, to a solution of silver nitrate; on heating to 460° it fuses to a dark-yellow liquid, which solidifies on cooling to a soft, colourless, tough mass. It was therefore called *luna cornea* by Oswald Croll (1608). Silver chloride volatilises at a white heat, giving the vapour density corresponding with AgCl. The fused chloride, according to Stas, is quite insoluble in cold water, but the curdy precipitate is slightly soluble (p. 359). The latter becomes powdery on standing in the liquid for a time. Silver chloride dissolves slightly in dilute nitric acid on standing; it dissolves in 200 parts of concentrated hydrochloric acid, is fairly easily soluble in sodium chloride, and readily in ammonia or sodium thiosulphate solution. The solution in ammonia contains complex ions: $Ag(NH_3)_2Cl \rightleftharpoons Ag(NH_3)_2^{\cdot} + Cl'$. Solid silver chloride absorbs ammonia, forming $AgCl,3NH_3$ and $2AgCl,3NH_3$ (p. 548). The thiosulphate solutions contain a very stable **silver sodium thiosulphate,** $AgNaS_2O_3$, which separates in crystals on evaporation. It possesses a strong sweet taste. If a solution of silver nitrate is added to one of sodium thiosulphate, and the liquid boiled, a black precipitate of silver sulphide is produced by the decomposition of the **silver thiosulphate,** which is transiently formed as a white precipitate:



$$SO_2\begin{cases}OAg\\SAg\end{cases} + \begin{cases}H\\OH\end{cases} = SO_2\begin{cases}OH\\OH\end{cases} + Ag_2S.$$

The insolubility of silver chloride provides a means for the **estimation of silver** (or of chlorides). The precipitate may be heated until it begins to fuse, and weighed, but as it tends to pass into a colloidal solution on washing, it is more convenient to adopt the **volumetric method**. No indicator is necessary if more than traces are present, as the curdy precipitate settles after the bottle containing the liquid has been violently shaken, and the silver nitrate solution ($N/10 = 16{\cdot}01$ gm. of $AgNO_3$ per litre) is added till a drop produces no further turbidity in the settled solution. Titration is carried out in a stoppered bottle covered with a roll of black paper, to prevent discoloration of the precipitate by light (p. 830). For the estimation of smaller amounts, a little potassium chromate is added to the *neutral* chloride solution before titration with silver nitrate; when all the chloride is precipitated, red **silver chromate,** Ag_2CrO_4, begins to be formed, giving a permanent brownish-red colour to the suspension. Another method is to add a little iron alum to the solution of the chloride *acidified* with nitric acid and titrate with ammonium thiocyanate. When the precipitation of the white curdy **silver thiocyanate**, AgCNS, is complete, ferric thiocyanate is formed which gives a red colour to the solution.

Silver bromide, AgBr, forms a pale yellow precipitate, insoluble (like the chloride) in dilute nitric acid, and only sparingly soluble in dilute ammonia. **Silver iodide**, AgI, is produced as a light yellow precipitate, quite insoluble in dilute nitric acid, and only very sparingly soluble in ammonia (which changes its colour to white).

Silver powder dissolves in aqueous hydriodic acid with evolution of hydrogen; on cooling, colourless crystals of AgI,HI separate, which rapidly decompose. AgI is dimorphous; the bromide and iodide melt at 426° and 556°, respectively. Silver iodide *contracts* on heating from

$-10°$ to 70° (Fizeau, 1876). Silver bromide does not absorb ammonia gas; it dissolves in liquid ammonia, and crystals of $AgBr,3NH_3$ separate, decomposing at 4° into $2AgBr,3NH_3$. The iodide forms $2AgI,NH_3$ with ammonia gas, and AgI,NH_3 with liquid ammonia.

If chlorine is passed into water containing an excess of silver oxide in suspension, silver chloride and free hypochlorous acid are first produced. (These are the only products if silver oxide is added to excess of chlorine water.) The hypochlorous acid reacts with the excess of silver oxide, forming a solution of **silver hypochlorite,** $AgClO$; the solution then does not smell of $HClO$, but is still an active bleaching agent:

$$Ag_2O \text{ (solid)} \rightleftharpoons Ag_2O \text{ (dissd.)} + H_2O \rightleftharpoons 2AgOH$$
$$AgOH + Cl_2 = AgCl + HClO.$$
$$AgOH + HClO = AgClO + H_2O.$$

In presence of silver oxide, the hypochlorite is fairly stable, but if the suspended solid is allowed to settle, the supernatant liquid rapidly deposits white silver chloride. The liquid loses its bleaching properties and now contains **silver chlorate,** $AgClO_3$, which may be crystallised out and dried in air at 150° (Stas): $3AgClO = 2AgCl + AgClO_3$. By reducing the chlorate in solution with sulphurous acid, silver chloride is formed: $AgClO_3 + 3SO_2 + 3H_2O = AgCl + 3H_2SO_4$.

Silver sulphate, Ag_2SO_4.—This salt is sparingly soluble in water, and is formed by boiling silver with concentrated sulphuric acid, or by precipitating a solution of the nitrate with sulphuric acid. It dissolves readily in dilute or concentrated sulphuric acid, or in dilute nitric acid. The **acid sulphate,** $AgHSO_4$, is formed in light yellow crystals when the sulphate is dissolved in less than three parts of sulphuric acid. **Silver sulphide,** Ag_2S, is formed when silver is heated with sulphur, or silver nitrate is precipitated with sulphuretted hydrogen.

The **disulphide,** Ag_2S_2, is formed by mixing solutions of sulphur in carbon disulphide and of silver nitrate in benzonitrile. **Silver sulphite,** Ag_2SO_3, is formed by precipitation; on heating to 100°, it forms the **dithionate**: $2Ag_2SO_3 = Ag_2S_2O_6 + 2Ag$.

Silver phosphates.—Silver orthophosphate, Ag_3PO_4, is formed as a pale yellow precipitate when a solution of sodium phosphate is added to one of silver nitrate. The reaction is usually represented by the equation:

$$3AgNO_3 + Na_2HPO_4 = Ag_3PO_4 + 2NaNO_3 + HNO_3,$$

but as the precipitate is readily soluble in nitric acid, only two-thirds of this amount of silver is precipitated:

$$6AgNO_3 + 3Na_2HPO_4 = 2Ag_3PO_4 + 6NaNO_3 + H_3PO_4.$$

The **acid phosphate**, Ag_2HPO_4, is deposited in white crystals from a solution of the phosphate in phosphoric acid. The **metaphosphate**, $AgPO_3$, and **pyrophosphate**, $Ag_4P_2O_7$, are gelatinous and crystalline white precipitates, respectively, formed by adding silver nitrate to the corresponding sodium salts. **Silver arsenite**, Ag_3AsO_3, and **silver arsenate**, Ag_3AsO_4, are canary-yellow and brick-red, respectively, and are formed by precipitation. The former dissolves in ammonia, and if the solution is boiled, silver is deposited.

Silver phosphide, AgP_2, is formed by the union of the elements at 400°. The **acetylide**, Ag_2C_2, is formed as an explosive white precipitate by passing acetylene into an ammoniacal solution of silver nitrate.

Photography.—The blackening of silver chloride on exposure to light was observed by Boyle, who explained it as due to the action of air. Scheele (1777) showed that if the blackened substance is digested with ammonia, unchanged silver chloride is dissolved and a residue of silver remains. He also noticed that the violet rays act most strongly on the chloride, whilst the red and orange rays have practically no action. Silver salts may be rendered sensitive to these rays by adding to them certain dyes (aurin, erythrosin, cyanin) which absorb light of these wave-lengths. These substances are called **photo-sensitisers**.

The first to turn the sensitive silver salts to account in making light pictures, or **photographs**, was Thomas Wedgwood (1802). In 1839 Daguerre allowed iodine vapour to act on a polished silver surface, which was exposed in the camera, and an invisible image was produced. The treated plate was exposed to mercury vapour, which condensed only on the portions which had been acted on by light, leaving the unaltered iodide in the shadows. The iodide was removed by a solution of sodium thiosulphate, as suggested by Herschel, and the picture thus **fixed**, or rendered non-sensitive to light. Archer (1851) used a transparent film of collodion (p. 570) spread on glass, and impregnated with zinc or cadmium bromide or iodide. This was treated before use by immersion in a solution of silver nitrate, when the halide was deposited. The plate was exposed in the camera whilst still wet, and then **developed** (Talbot, 1841) by immersion in a solution of a reducing agent such as ferrous sulphate, or pyrogallic acid, which converted the *altered* halide into black metallic silver. The *unaltered* halide was then dissolved out by potassium cyanide or sodium thiosulphate, and a **negative** produced, in which the light and shade in the picture are reversed. To obtain a **positive**, the plate is laid on a piece of paper coated with silver chloride, and then exposed to light. The **print** is fixed in the same way as the plate; it is not developed, as the chloride can be directly changed sufficiently in colour to give the requisite shades.

In the modern **dry-plate process**, an emulsion of silver bromide is prepared by adding ammoniacal silver nitrate to a solution of gelatin in hot water containing potassium bromide. The emulsion, after "ripening" at 45° for some time, whereby the halide grains, at first of diameter 0·001 mm., grow to 0·003 mm., is poured in a thin film on a glass plate or celluloid film. The soluble salts are washed out after setting, and the film dried, all operations being carried out in the dark or in orange light. After exposure (which may only be a fraction of a second), the plate is developed with pyrogallol, hydroquinone, or metol (paramethylaminophenol) in presence of alkali. These substances are oxidised, and the silver bromide which has been changed by light is reduced to metallic silver, *e.g.*,

$$\underset{\textbf{Hydroquinone}}{C_6H_4(OH)_2} + 2AgBr = \underset{\textbf{Quinone}}{C_6H_4O_2} + 2Ag + 2HBr$$

To prevent over-vigorous development, when some of the unchanged bromide is reduced and leads to "fogging" of the plate, a **retarder,** consisting of potassium bromide, is added to the developer. After washing, the plate is fixed in sodium thiosulphate. The **print,** or positive, is made on silver chloride paper, coated with albumin, which is **toned** after exposure by immersion in a solution of gold chloride (brown tone), or platinic chloride (grey tone), a little of the silver being dissolved and replaced by the nobler metal. It is then fixed in thiosulphate.

A print may also be made on silver bromide paper (**velox,** or **gaslight paper**), which is exposed in the same way as a plate, and developed. The gelatin in the plate and the albumin on the paper act as **sensitisers** to the silver salt, accelerating the action of light upon it.

The exact mechanism of these photochemical changes is still obscure. According to one theory, a **sub-halide,** *e.g.*, Ag_2Br, is formed by loss of halogen, which is absorbed by the sensitiser. But hydrobromic acid is never detected in the gelatin, the whole of the bromine passing into the developer. Pure dry silver chloride does not blacken on exposure to light, and the ordinary salt always takes up oxygen as it loses chlorine, so that it has been suggested that an **oxy-chloride** is produced, Ag_2ClO. Recent work points, however, to a purely **physical explanation** (Joly, 1905). Halides of silver on exposure to light emit electrons, and the photo-sensitiveness is in the proportion of the order of the **photo-electric activity**: $AgBr > AgCl > AgI$. Cathode rays (free electrons), and *X*-rays (which produce free electrons from matter) also produce photographic effects. The molecules of halide which have lost an electron are supposed to be those capable of being developed. Scheele's original experiments, however, prove conclusively that chemical reactions occur when the action of light is prolonged.

GOLD. $Au = 195{\cdot}6$.

Gold.—Gold, by reason of its occurrence in the free state, and of its beautiful colour and brilliance, was probably the first metal known to man. Gold ornaments are found in neolithic remains. Because of its supposed perfection, the metal was associated by the alchemists with the sun, was called *Sol*, and represented by the symbol ☉, or ☼. The alchemists considered that the other metals, if suitably purified, or " cleansed," could be transmuted into gold.

A typical description of the art of making gold, as understood by the alchemists, is the following from Philalethes, " Secrets Revealed in Chymistry " (1669): " That thou mayest have this knot well unfolded, attend diligently. Let there be taken of our Fiery Dragon, which hides the magical Chalybs in his own belly, 4 parts ; of our Magnet 9 parts ; mix them well together with a torrid Vulcan, or great fire, in the form of a mineral water, upon which there will swim a scum, which is to be cast away ; remove the shell and then the kernel, purge it the third time with Fire and Salt, which will easily be done if Saturn shall have beheld himself in the looking glass of Mars. Thence is made the Chameleon, or our Chaos in which all Arcana's lies hid virtually but not actually." The author adds: " None ever wrote so clearly." It is instructive to compare this with the " Sceptical Chymist " of Robert Boyle, published in the same year : " For Quicksilver, with several Metals, will compose an Amalgama ; and with divers Menstruums, it seems to be brought into the form of a Liquor ; and with Aqua-Fortis, it may be turned either into a white or into a Red Precipitate ; with Oyl of Sulphur, into a pale Yellow one ; with Sulphur it will compose a red, and Volatile Cinabar : With some Saline Bodies, it will ascend in the form of White Salt, Dissoluble in Water ; with Regulus of Antimony, and Silver, it may be Sublimed into Chrystal : and . . . yet out of all these Substances, it may be again Obtained, and Reduced to its Pristine Form." There is nothing in this description which cannot be followed by the modern chemist.

Gold occurs usually in the native condition, alloyed with a certain amount of silver, and sometimes copper and traces of platinum. Some tellurium compounds of gold occur in small amounts (p. 531), and traces of gold are found in pyrites and other ores, and in sea-water. Gold is recovered from burnt pyrites, but a sea-weed which collects gold instead of iodine is yet unknown. The **native gold** occurs in quartz veins or reefs intersecting metamorphic rocks of the chlorite type, such as occur in Wales, where gold extraction is carried on to a small extent. The most important European localities where gold is found are Russia, Hungary, and Germany. Hungarian gold may contain tellurium, which must be separated if the metal is to be used for dental purposes. Gold occurs all over Asia. The Russian mines of the Urals, discovered in 1819, supplied most of the metal until the accidental discovery of gold in California in 1849. The richest fields are in Africa, especially the Transvaal

Rand (which supplied 8,237,700 oz. in 1911, and gives the highest production in the world) and in Australia. In North America the fields extend from Mexico to Klondike, the latter field being opened in 1896.

Metallurgy of gold.—Native gold occurs either as *nuggets* of varying size (one of 184lb. weight was found at Ballarat) in the rock, or as *grains* in the alluvial sand. From the latter it is extracted by washing away the lighter sand in agitating cradles or sluices, or breaking up the auriferous gravel by powerful jets of water, under 100–300ft. head. The rock is crushed in batteries of stamping mills, and mercury is added to the resulting slime to amalgamate with the gold. The gold amalgam is retained by amalgamated copper plates. The residual slime ("tailing") is treated by the cyanide process (*q.v.*). The amalgam is scraped off the plates, distilled in iron retorts, and the residue cupelled (p. 819).

To extract gold from auriferous pyrites, obtained from the rock as so-called "concentrates," they are treated by Plattner's **chlorine process**. The roasted pyrites are moistened with water in tubs with false-bottoms, and impregnated with chlorine gas. After 24 hours the soluble **gold trichloride,** $AuCl_3$, is leached out with water, and the gold precipitated by ferrous sulphate. The reaction is one of simultaneous oxidation and reduction : $AuCl_3 + 3FeSO_4 = Au + FeCl_3 + Fe_2(SO_4)_3$, or, more simply : $Au^{\cdot\cdot\cdot} + 3Fe^{\cdot\cdot} = Au + 3Fe^{\cdot\cdot\cdot}$. Bromine water has also been used.

Gold is now extracted on a large scale from the tailings from stamp-mills or directly from the finely stamped ore by the **cyanide process** of MacArthur and Forrest. The slimes are agitated in large tanks with a solution of cyanide containing 0·3 per cent. of KCN, in which the gold dissolves. After settling, or filter-pressing, the clear liquor is reduced by adding metallic zinc (of which metal the packages for the export of the cyanide are made). The precipitate is fused with lead and the alloy, containing 10 per cent. of gold, is cupelled. The reactions in the cyanide process are somewhat complicated ; they occur in presence of atmospheric oxygen, and hydrogen peroxide is formed (p. 342) by **autoxidation :**

$$2Au + 4KCN + 2H_2O + O_2 = \underset{\substack{\text{Potassium}\\ \text{aurocyanide}}}{2KAu(CN)_2} + 2KOH + H_2O_2$$

$$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH.$$

The reduction process is : $2KAu(CN)_2 + Zn = K_2Zn(CN)_4 + 2Au$. In this way quartz containing only half an ounce of gold per ton can be profitably treated.

Gold refining.—The gold bullion is then **refined.** If it contains copper, this is removed by an oxidising fusion with borax and nitre. The silver and gold are separated by granulating the alloy, and boiling with concentrated sulphuric acid, which extracts the silver as sulphate, leaving the gold (Scheele, 1753). The alloy must not contain more than 33 per cent. of gold, otherwise the silver is not dissolved. If it contains more gold than this the alloy is melted with silver until it contains about one-quarter its weight of gold. This operation of separation is termed **quartation.** In the new **electrolytic process** of Wohlwill (1910), the bullion is made the anode in a solution of 2·5–6 per cent. of gold chloride, containing 2–5 per cent. of hydrochloric acid, and an alternating current is superposed on the direct electrolysing current. In the **Rose process** (1910) the zinc precipitates are fused, and air or oxygen is blown through, when the baser metals oxidise in succession and pass into a borax-silica flux.

Standard gold.—Pure gold is too soft for use as ornaments or for coinage, and it is alloyed with copper, or silver, or both. The copper makes the colour redder (English gold coin), silver imparts a pale colour (Australian gold coin). The *fineness* is expressed either in parts per 1000, or in *carats*, pure gold being 24 carat fine, and five standard alloys of 22, 18, 15, 12, and 9 carat, *i.e.*, parts of gold in 24 of alloy, are legalised. The 22 carat English gold coin has a fineness of 916·67. German, Italian, and American coinage has a fineness of 900, *i.e.*, 21·6 carat. The presence of 1 part of bismuth in 1920 parts of gold renders the metal brittle.

Gold plating is carried out in the same way as silver plating, by electro-deposition from solutions of gold cyanide in potassium cyanide, the requisite amounts of silver and copper salts being added. These metals are deposited as an alloy with the gold if a suitable voltage is used.

Properties of gold.—Gold is a bright yellow metal, which crystallises (like most metals) in the regular system ; it has a high density (19·32), and is a good conductor of heat and electricity. It melts at 1064°, expanding on fusion, and forms a bluish-green liquid (*cf.* copper, p. 810). It volatilises appreciably 100° above its melting-point, and boils at about 2500°. It is the most ductile metal, as was stated by Pliny, and can be beaten into leaves 0·0005 mm. thick. The deposits on gold lace are only 0·000002 mm. thick. By treating gold leaf with a solution of potassium cyanide, Faraday obtained films 0·0001 mm. thick, which transmit green light. On heating gold-leaf the metal crystallises and minute gaps are formed, which transmit red light, as does ruby-glass (*q.v.*). Gold is not attacked by oxygen or any single acid except selenic, but it dissolves in solutions of chlorine, bromine, or iodine, and therefore in *aqua regia*. Fused alkalies and nitrates, and a solution of ferric bromide, also attack it.

Colloidal gold is formed by Bredig's process (p. 824), or by reducing solutions of gold chloride with phosphorus, ferrous sulphate, hydrazine, formaldehyde, etc. The different solutions have different colours according to the sizes of the colloidal particles. Those with larger particles are blue; with decreasing size the colour passes through a fine ruby-red to yellow, and approaches that of gold chloride, containing gold atoms, in an unbroken chain of perfect continuity. This indicates that there is no fundamental difference between colloidal and true solutions. By precipitating a mixture of gold, stannous, and stannic chlorides, with alkali, a purple powder, called **purple of Cassius** (discovered by Andreas Cassius, and described by his son in 1685), used for making ruby glass, is thrown down. It appears to be a colloidal form of tin oxide with adsorbed colloidal gold (Moissan, 1905). When glass is fused with purple of Cassius and annealed, it assumes a fine ruby colour, due to the presence of ultra-microscopic particles of gold. Gold differs from copper and silver in the extreme ease with which its compounds are reduced to the metal.

Compounds of gold.—If gold is dissolved in *aqua regia* it forms a bright yellow solution, which on evaporation deposits deliquescent yellow crystals of **chlorauric acid,** $HAuCl_4,3H_2O$, commonly known as "gold chloride." The solution is reduced to metallic gold by hydrogen gas or exposure to light. If gold is dissolved in chlorine water, the solution evaporated, and the residue heated to 150°, a brown, crystalline mass of **auric chloride,** $AuCl_3$, is left, soluble in water, alcohol, and ether. On heating $AuCl_3$ at 175° it gives off chlorine and leaves a yellow powder of **aurous chloride**, AuCl, which at higher temperatures decomposes into chlorine and gold. AuCl is decomposed by water: $3AuCl = AuCl_3 + 2Au$. Chlorauric acid, when evaporated with a solution of potassium chloride, gives red crystals of the potassium salt $2KAuCl_4,H_2O$. On heating, these form the **chloraurite,** $KAuCl_2$. If AuCl is treated with cold dilute potash, a violet powder of **aurous oxide**, AuO, is left. By precipitating chlorauric acid with potash, **auric hydroxide,** $Au(OH)_3$, is obtained. This is a weak base, and also dissolves in caustic potash, the solution depositing **potassium aurate,** $KAuO_2,3H_2O$, on evaporation *in vacuo.* The hydroxide when gently heated forms **auric oxide,** Au_2O_3, which at a higher temperature readily decomposes into oxygen and the metal. **Auric bromide**, $AuBr_3$, is formed by dissolving gold in bromine water; if gold is heated with iodine at 50–114°, **aurous iodide,** AuI, is formed. On precipitating gold chloride with potassium iodide, a green precipitate of **auric iodide**, AuI_3, is first formed, which quickly decomposes into the aurous compound and iodine (*cf.* copper).

The **sulphides,** Au_2S and AuS, are formed when H_2S is passed into solutions of potassium aurocyanide (afterwards acidified), and a cold neutral solution of $AuCl_3$, respectively: $8AuCl_3 + 9H_2S + 4H_2O =$

$8AuS + 24HCl + H_2SO_4$. Au_2S_3 is not formed in the latter reaction, but is produced when anhydrous lithium aurichloride is treated with H_2S at —10°.

By fusing gold with sodium sulphide and sulphur, it forms a substance soluble in water, and by evaporation in a vacuum colourless crystals of **sodium aurosulphide,** $NaAuS,4H_2O$, are deposited. Stahl suggested that this was the method used by Moses in reducing the Golden Calf to a potable form for the consumption of the Israelites. From a solution of auric chloride in sodium thiosulphate, colourless crystals of **Fordos and Gélis' salt,** $Na_3Au(S_2O_3)_2,2H_2O$, separate. This substance is not reduced by ferrous sulphate.

Fulminating gold, or **auro-diamine,** $AuHN{\cdot}NH_2$, is prepared by digesting precipitated auric hydroxide with ammonia; it is a dirty olive-green powder which when dry explodes with great violence when heated or struck. It is decomposed by hydrochloric acid: $AuN_2H_3 + 5HCl = AuCl_3 + 2NH_4Cl$. By the action of ammonia on aurous oxide, $NAu_3{\cdot}NH_3$ (**sesquiaurammine**) is formed, which on boiling with water forms **gold nitride,** Au_3N.

An important compound of gold is **potassium aurocyanide,** $KAu(CN)_2$, used in electro-plating. This is produced by dissolving fulminating gold in boiling potassium cyanide solution. On cooling colourless lustrous crystals separate. From the solution hydrochloric acid precipitates yellow **aurous cyanide,** AuCN. Auric cyanide, $Au(CN)_3$, is not known, but **potassium auricyanide,** $KAu(CN)_4$, also used in electro-gilding, is obtained in colourless crystals by mixing hot concentrated solutions of gold trichloride and potassium cyanide.

A delicate **test for gold** is the purple precipitate formed by pouring the solution into concentrated stannous chloride solution (1 part of gold in 100 million parts of water can be detected).

The **atomic weight** of gold has been found by the analysis of potassium auribromide K_2AuBr_4, and other salts. The accepted value is 195·6 (H = 1).

EXERCISES ON CHAPTER XXXIX

1. Give a general description of the properties of the metals: copper, silver, and gold, with special reference to their position in the Periodic System.
2. In what forms does copper occur, and how is the metal obtained?
3. What alloys of copper, silver, and gold are used, and for what purposes?
4. How are the following prepared from metallic copper: cupric oxide, cuprous chloride, cupric sulphate? What are their properties?
5. How are cuprous oxide, cuprous sulphate, and cuprammonium sulphate prepared?
6. What is the action of (*a*) potassium iodide, (*b*) potassium cyanide,

(*c*) ammonium thiocyanate, on a solution of cupric sulphate ? Give equations.

7. Give a brief account of the occurrence and metallurgy of silver. How would you obtain a specimen of pure silver from an alloy with copper ?

8. Describe the preparation and properties of (*a*) colloidal silver, (*b*) silver oxides, (*c*) fulminating gold, (*d*) gold ruby-glass, (*e*) silver sulphate, (*f*) gold trichloride.

9. How have the atomic weights of silver and gold been determined ? Why is the atomic weight of silver of great importance in connection with those of other elements ?

10. What chemical reactions occur in photography ? How are photographic plates prepared ?

11. How are silver- and gold-plating carried out electrolytically ? What is electrotyping ?

CHAPTER XL

THE ALKALINE-EARTH METALS

Metals of the alkaline earths.—The elements of **Group** II in the Periodic Table are all metals. They are divided into two **sub-groups,** the odd series and the even series :—

(*a*) **Even series :** the **metals of the alkaline earths :** calcium, strontium, barium, and radium.

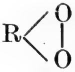
(*b*) **Odd series :** beryllium, magnesium, zinc, cadmium, and mercury.

With the possible exception of mercury, all these metals are *bivalent* in all their compounds : RX_2. The mercurous salts, such as calomel, HgCl, in which the metal seems to be univalent, probably have the doubled formulæ Hg_2X_2, in which the group —Hg—Hg—, made up of two bivalent mercury atoms, is also bivalent. All these metals form **basic oxides**, RO, and (except mercury) **hydroxides,** $R(OH)_2$. There is a regular gradation in the solubility of these hydroxides in series (*a*) ; those of series (*b*) are practically insoluble in water. The same holds for the **chlorides**, RCl_2, of sub-group (*a*) :—

Grams dissolved by 100 gm. of water :

$Ca(OH)_2$	0·29 at 10°	$CaCl_2$	74·5 at 20°
$Sr(OH)_2$	0·92 ,,	$SrCl_2$	53·9 ,,
$Ba(OH)_2$	3·9 ,,	$BaCl_2$	35·7 ,,

The older chemists gave the name **earth** to all non-metallic substances insoluble in water and unchanged by fire. Lime and magnesia were found to have an alkaline reaction, and were called **alkaline earths**, the name being afterwards applied to baryta (Scheele, 1774), and strontia (Hope, 1792). The metals themselves were isolated by Davy (1807) by electrolysis, following a suggestion by Lavoisier that, like other "bases," they were oxides of metals. Magnesium is now usually placed in sub-group (*b*).

The **metals of the alkaline earths** are all silver-white, oxidise in the air, and decompose water, though less vigorously than the alkali-metals sodium, potassium, etc. They form, in addition to the **basic oxides**, RO, true **peroxides,** RO_2, in which the metal is still bivalent : $R\langle O_2$. They unite directly with hydrogen and with nitrogen, forming **hydrides,** RH_2, and **nitrides,** R_3N_2, respectively. The compounds give distinctive colours when heated on platinum wire, moistened with hydrochloric acid, in the Bunsen flame: calcium, orange-red; strontium, crimson; barium, apple-green.

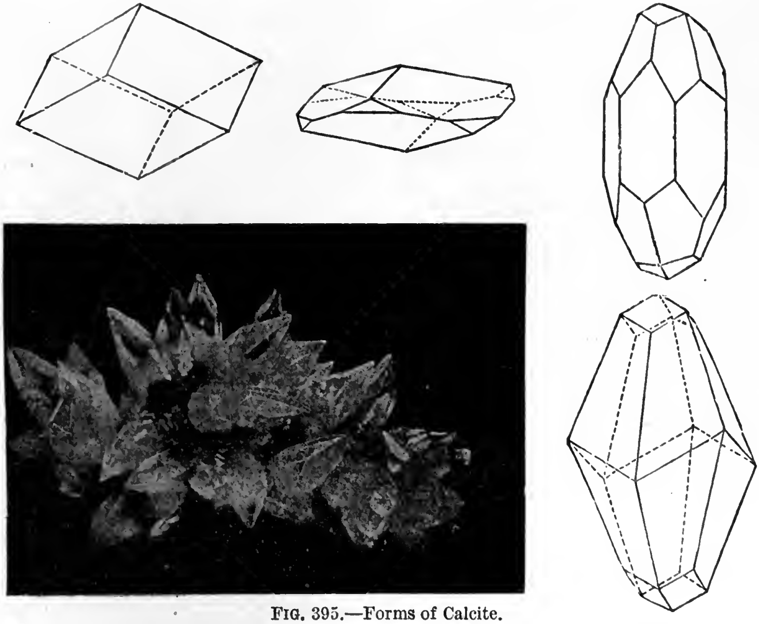


FIG. 395.—Forms of Calcite.

CALCIUM, Ca=39·75.

Limestone. — The most abundant mineral of calcium is the **carbonate**, $CaCO_3$, which is dimorphous, crystallising in various forms of the hexagonal system as *calcite* (Fig. 395), and in the rhombic sys-

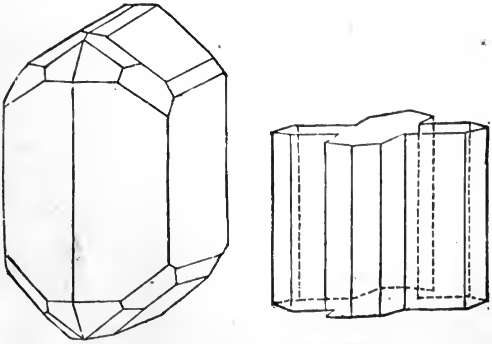


FIG. 396.—Crystals of Aragonite.

tem as *aragonite* (Fig. 396). The former is the commoner form; besides occurring in minerals, it forms the chief constituent of egg-shells, bones (together with calcium phosphate), oyster-shells, and coral, all of which effervesce with acids. In the massive form it occurs as *marble, limestones* of various kinds, *calc-spar* (a very pure transparent variety of which is Iceland spar), and *chalk*. Chalk consists of the shells of minute marine organisms. In combination with magnesium carbonate, it forms *dolomite*, $MgCO_3,CaCO_3$, of which (as well as limestone) whole mountain-chains are composed.

If carbon dioxide is passed through cold lime-water, the amorphous flocculent precipitate which first appears soon becomes crystalline, and has the form of calcite. If the lime-water is hot, crystals of aragonite are produced. Calcite is the stable form at the ordinary temperature; at 470° it is converted into aragonite. A third form, μ-$CaCO_3$, is said to be precipitated at 60°. The solubility of calcium carbonate in water containing carbonic acid has already been described (p. 205). By adding a solution of $KHCO_3$ to a cooled solution of $CaCl_2$, a white precipitate of $Ca(HCO_3)_2$ is formed.

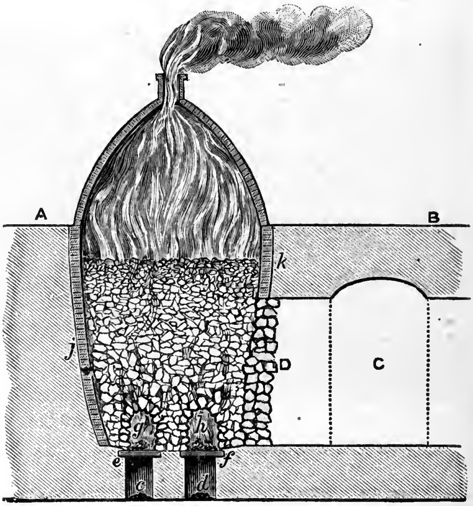


FIG. 397.—Derbyshire

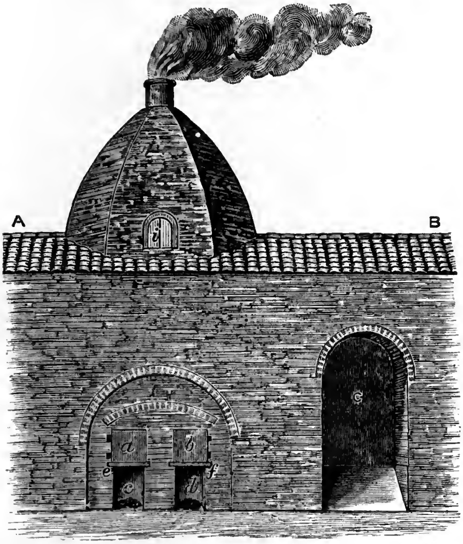
Quicklime, CaO.—If calcium carbonate is heated to dull redness (550°), it begins to decompose, evolving carbon dioxide, and leaving **calcium oxide**, or **quicklime**, CaO. In a closed vessel, the decomposition stops at a certain pressure of the carbon dioxide, known as the **dissociation pressure**, which has a definite value at each temperature; the system is then in equilibrium: $CaCO_3 \rightleftharpoons CaO + CO_2$.

The dissociation pressure at various temperatures is given below; it increases rapidly with the temperature:

t°	700°	750°	800°	850°	900°
P_{CO_2} mm. Hg.	50	99	195	370	700

If the carbon dioxide is swept away by a current of air, dissociation goes on till the reaction is practically complete. This is applied in the manufacture of quicklime from limestone or marble. The process is known as **lime-burning.**

In some districts, *e.g.*, in High Peak, Derbyshire, the **limekiln** is filled with blocks of the limestone, and an arch of lumps of the stone is built over the fire below, the fuel being kept separate from the stone (Fig. 397). The burning goes on for thirty-six to forty-eight hours, when the kiln is allowed to cool, and the lumps of quicklime (which is then nearly pure—" Buxton lime " contains 98 per cent. of CaO) are removed. This process is wasteful in fuel, and on the Continent **continuous limekilns** (Fig. 398) are used. The broken stone is mixed with about 20 per cent. of its weight of coke or coal, and is fed intermittently into a shaft kiln through a cup-and-cone arrangement, *a*, *b*. The coke burns, and the CO_2 produced from the $CaCO_3$, mixed with nitrogen, passes out through *d*. The lime works its way gradually down the kiln, and is withdrawn through apertures, *e* at the base. It contains the fuel ashes, and is therefore less pure than that made in intermittent kilns.



Lime Kiln.

Pure calcium oxide is prepared by heating Iceland spar with the blowpipe in a platinum crucible, with free access of air, until a little of the white opaque residue, after cooling and addition of water, no longer effervesces with acid. It is a white, amorphous mass, sp. gr. 3·3, which melts at about 1900° and can be boiled in the electric furnace, the vapour condensing in cubic crystals. Lime resists the temperature of the oxy-hydrogen blowpipe without more than sintering, and is therefore used in making furnaces for fusing platinum. These consist (Fig. 399) of two blocks of lime, hollowed out, in the lower one of which the metal is placed, whilst the blowpipe is introduced through a hole in the upper block. The electric furnace used by Moissan (Fig. 400) was also constructed of lumps of quicklime.

Slaked lime, $Ca(OH)_2$.—If quicklime is moistened with water, much heat is evolved, and clouds of steam are given off. (Gunpowder may be kindled by strewing a little over the mass.) The lime combines with the water, cracks, and finally, after addition of sufficient water, crumbles down to a fine, dry, white powder. This is **calcium hydroxide**, $Ca(OH)_2$, known as *slaked lime*. If mixed with an excess of water a paste, called *milk of lime*, is formed ; if shaken with water it dissolves sparingly, producing *lime-water* (2·2 gm. of CaO per litre at 10°). The solubility, as Dalton found, decreases with rise of temperature (p. 99). Calcium hydroxide is also formed as a white precipitate by adding caustic soda to a concentrated solution of calcium chloride: $CaCl_2 + 2NaOH = Ca(OH)_2 + 2NaCl$. With saturated solutions the mixture becomes solid (" the chemical miracle " of Francisco Lana, 1686). Six-sided crystals of calcium hydroxide are deposited by evaporating lime-water in a vacuum over sulphuric acid. Slaked lime, when heated to dull redness, loses water, and is converted into quicklime.

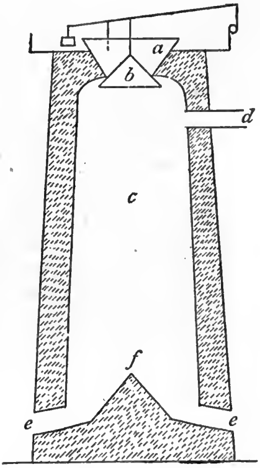


FIG. 398.—Continuous Lime Kiln.

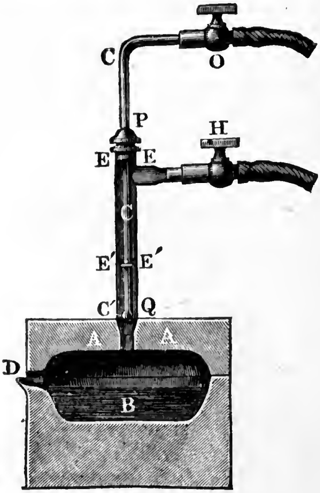


FIG. 399.—Oxyhydrogen Blow Pipe Furnace with Lime Crucible.

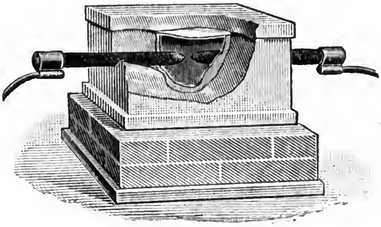


FIG. 400.—Moissan's Electric Furnace.

Quicklime, when exposed to the air, slowly absorbs moisture and carbon dioxide, crumbling to a powder which consists of a mixture of hydroxide and carbonate. Pure lime does not absorb perfectly dry carbon dioxide. Lime-water on exposure to air becomes covered with a crust of calcium carbonate. If this is broken it falls to the bottom, and another appears. In this way the whole of the lime is precipitated.

Lime is used chiefly in the preparation of **mortar,** for building purposes, this consisting of a thick paste of slaked lime with three to four times as much sand as quicklime originally taken. Lime made from magnesian limestone slakes slowly and is called "poor lime," distinguished from "fat lime," which slakes easily. The hardening of mortar consists in the evaporation of the moisture, or its absorption by the bricks, and the slow conversion of the hydroxide into calcium carbonate by atmospheric carbon dioxide; slight combination between the lime and the silica of the sand also occurs. Modern mortar usually contains ground cinders and rubbish; soluble salts from these form an efflorescence on the bricks, consisting chiefly of sodium sulphate.

Calcium peroxide is formed as a hydrate, $CaO_2,8H_2O$, by precipitating lime-water with H_2O_2. From very concentrated solutions at 0°, or in all cases above 40°, anhydrous CaO_2 is precipitated. Calcium peroxide is manufactured for use as an antiseptic by compressing slaked lime and Na_2O_2, and washing with ice-water. Much free lime is present in it. It is not formed directly from CaO and O_2 (*cf.* BaO_2).

Cement.—If limestone containing more than 5 per cent. of clay is burnt, the resulting lime forms a mortar which hardens under water, and is therefore called **hydraulic mortar.** The old Roman mortar was of this type, and many buildings constructed with it are still standing firm. In 1796 J. Parker prepared a similar **Roman cement** by heating clay and limestone. **Portland cement** is made by burning a mixture of limestone and clay, either mixed with coal as in lime-burning, or by feeding the mixture into the top of a revolving tubular furnace inclined at an angle, into the lower part of which a blast of air charged with coal-dust, which forms an intense flame, is injected. The *cement-clinker* so produced is ground to powder, and packed in air-tight barrels.

The constitution of cement, and the mechanism of setting, have been variously explained. Cement clinker appears to contain the following compounds:

tricalcium silicate,	$3CaO,SiO_2$
tricalcium aluminate,	$3CaO,Al_2O_3$;
calcium orthosilicate,	$2CaO,SiO_2$
pentacalcium trialuminate,	$5CaO,3Al_2O_3$.

A certain amount of free lime, CaO, is also present. According to other investigators, tricalcium aluminate is a solid solution of lime in pentacalcium trialuminate. On addition of water, the calcium aluminates are first hydrated, then the silicates take up water. During this process free lime is separated as calcium hydroxide. Le Chatelier regarded the final compounds as $2CaSiO_3,5H_2O$, and $4CaO,Al_2O_3,12H_2O$, unstable supersaturated solutions of the basic silicates being initially formed, which rapidly crystallise in the form of a mass of interlacing needles of the basic silicate. Michaelis, however, considered that the compound $2CaSiO_3,5H_2O$ is produced in the first instance as a colloidal jelly, the gradual dehydration of which leads to the hardening of the cement. The formation of colloidal material in the early stages of the setting has been confirmed.

A mixture of cement and broken bricks or gravel forms *concrete*; *reinforced concrete* is concrete cast over a steel framework.

Calcium chloride, $CaCl_2$.—If limestone or marble is dissolved in hydrochloric acid, a solution of **calcium chloride,** $CaCl_2$, is formed. This usually contains ferric chloride as an impurity, and is yellow. A little chlorine water is added to oxidise any ferrous iron, then the solution is filtered, and milk of lime added until the liquid is slightly alkaline. On boiling, ferric hydroxide is precipitated; if the filtered liquid is neutralised with pure hydrochloric acid and evaporated to a syrupy consistency, colourless very deliquescent crystals of the hexahydrate, $CaCl_2,6H_2O$, m.-pt, 30° separate. These dissolve in water with considerable lowering of temperature; the eutectic point is — 55°. On heating the crystals to 200°, water is evolved, and a white, porous mass of the dihydrate, $CaCl_2,2H_2O$, remains, which is used for preparing solutions for refrigerators. If heated strongly, a porous mass of the anhydrous salt is formed, which is used in drying gases, etc. This fuses at 780°, and forms a hard crystalline mass on cooling. The dihydrate and the anhydrous salt evolve heat when dissolved in water. Calcium chloride dissolves readily in alcohol. Anhydrous calcium chloride absorbs ammonia gas, forming the unstable compound $CaCl_2,8NH_3$.

If a solution of 120 parts of $CaCl_2$ in 100 parts of water is cooled to 18–38°, a tetrahydrate, $CaCl_2,4H_2O$, separates, which exists in two forms, α and β. At 45·3°, the stable α form gives $CaCl_2,2H_2O$; at 177·5°, $CaCl_2,H_2O$ separates from the solution; and at 260°, anhydrous $CaCl_2$ (Roozeboom, 1889).

Large quantities of calcium chloride are formed as a by-product of the Ammonia-Soda process (p. 782); a solution of it is used in refrigerating plants ("brine"), since it freezes only at a low temperature; and also, on account of the deliquescent character of the salt, for preventing dust on roads.

Homberg (1693) observed that freshly-fused calcium chloride is **phosphorescent**; Baldwin (1674) had noticed the same property with calcium nitrate. Perfectly pure salts are not phosphorescent; the property is due to the presence of traces of heavy metals, such as bismuth.

Calcium fluoride, CaF_2, or *fluor-spar* (m.-pt. 1330°) (p. 415) is nearly insoluble; the **bromide,** $CaBr_2$ (m.-pt. 765°), and **iodide,** CaI_2 (m.-pt. 740°), are similar to the chloride.

Metallic calcium.—Metallic **calcium** is now prepared on a technical scale by the electrolysis of a mixture of 100 parts of calcium chloride and 16·5 parts of fluor-spar, fused at 660° in a bath formed of blocks of carbon. The cathode is an iron rod, which touches the surface of the fused chloride (Fig. 401). The cathode is slowly screwed up as the calcium accumulates, and the metal is drawn out into the form of an irregular rod, 20–30 cm. in diameter, protected from oxidation by a layer of chloride. The metal (sp. gr. 1·55) melts at 810°, and readily sublimes in a vacuum below this temperature. It is malleable, burns brightly in oxygen, combines with sulphur, chlorine, nitrogen, etc., and reduces nearly all metallic oxides on heating. It reduces sodium chloride at 800°.

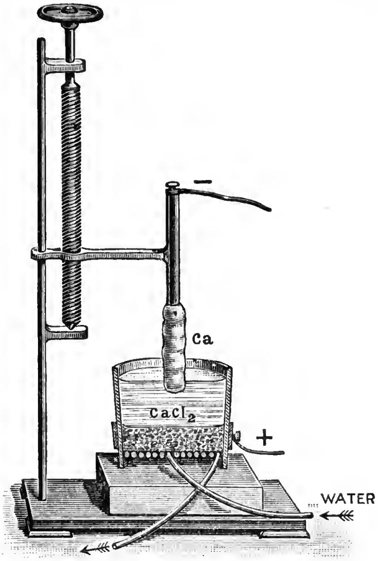


FIG. 401.—Manufacture of Calcium by Electrolysis.

Calcium is used in freeing absolute alcohol from the last traces of water. The liquid is digested with calcium turnings, when a somewhat violent reaction occurs. A little phosphorus pentoxide is added to the clear liquid, to combine with traces of ammonia (formed from the nitride, Ca_3N_2), and the alcohol is distilled.

If calcium is heated in a tube connected with a nearly evacuated vessel, it absorbs the last traces of air, forming CaO and Ca_3N_2, and a very high vacuum is produced. Heated calcium is used in separating argon from nitrogen (p. 600).

By heating calcium and calcium chloride in a steel cylinder to 1000°, red crystals of the **subchloride,** CaCl, are formed. CaF and CaI are also known.

By passing hydrogen and nitrogen over heated calcium, the **hydride** (" hydrolith," p. 183), CaH_2, and **nitride,** Ca_3N_2, respectively are formed. The hydride, which is formed at 400–500° with incandescence, is colourless ; the nitride is brownish-yellow ; both are crystalline. On passing steam over the nitride, ammonia is produced : $Ca_3N_2 + 6H_2O = 3Ca(OH)_2 + 2NH_3$. Ammonia gas is absorbed by calcium with formation of $Ca(NH_3)_4$ and evolution of heat. This ignites in air ; in absence of air it forms $Ca(NH_2)_2$.

Calcium sulphate, $CaSO_4$.—**Calcium sulphate,** $CaSO_4$, occurs as **anhydrite** along with limestone or rock-salt, or more commonly as the di-hydrate *gypsum*, $CaSO_4,2H_2O$, which forms transparent crystals called *selenite* (Fig. 402, often twinned), or occurs in crystalline masses, either fibrous (*satin spar*) or opaque (*alabaster*). Anhydrous calcium sulphate exists in two forms ; (*a*) natural anhydrite and the substance formed by dehydrating gypsum at a red heat, both practically insoluble ; (*b*) a soluble form, " setting " with water, produced by dehydrating gypsum at 60–70° in a vacuum over P_2O_5. Gypsum can easily be reduced to an extremely fine powder, and the solubility increases with the fineness of the grains. This is a general result, and is due to surface-tension forces, which are more pronounced with small particles. The solubility of gypsum increases with rise of temperature to 40°, and then diminishes at higher temperatures.

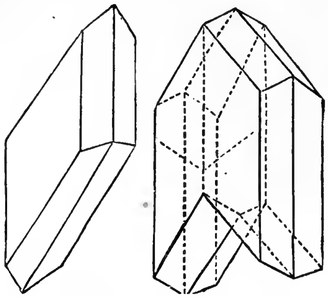


FIG. 402.—Gypsum Crystals.

If gypsum is heated to 120–130° it loses water and forms **plaster of Paris,** the hemihydrate, $2CaSO_4,H_2O$, which when mixed with water evolves heat, and quickly solidifies, expanding slightly ; it is therefore used for making plaster casts in moulds. If the surface is painted with a solution of paraffin wax in petrol, the wax fills the pores, and an ivory-like surface is produced. Plaster of Paris, if heated at 140°, begins to lose water ; the whole of the water is rapidly expelled at 200° ; the residue of anhydrous $CaSO_4$ rapidly takes up water, but if the heating has been more intense the residue hydrates only very slowly, and is said to be *dead-burnt.* By heating to 400°, slight decomposition into CaO and SO_3 occurs and the German plaster called **Estrich-gips,** which sets slowly, and produces a smooth, hard surface, used for floors, walls, etc., is formed.

Precipitated gypsum is formed by adding sulphuric acid to a solution of calcium chloride. It is used under the name of *pearl-hardening* for adulterating (" filling ") glazed paper. Barium sulphate is used for a similar purpose, giving a very heavy paper.

The double salts, $CaSO_4,K_2SO_4,H_2O$ (*syngenite*), $CaSO_4,Na_2SO_4$ (*glauberite*), and $CaSO_4,2Na_2,SO_4,2H_2O$, are known. Calcium sulphate dissolves in a concentrated solution of ammonium sulphate, forming $CaSO_4,(NH_4)_2SO_4,H_2O$. Strontium and barium sulphates are insoluble.

Calcium sulphite, $CaSO_3,2H_2O$, is formed as a white precipitate by passing sulphur dioxide through lime-water, or adding a solution of a sulphite to one of calcium chloride. It dissolves in aqueous sulphurous acid, forming a solution known as **calcium bisulphite,** $Ca(HSO_3)_2$; this is prepared by passing sulphur dioxide in excess, through milk of lime; it is used in sterilising beer casks, and in the manufacture of wood-pulp.

Wood consists of *cellulose* and *lignin*, the latter soluble in boiling bisulphite solution. The cellulose is left, and is used for making paper. The pulp is bleached by chlorine, the excess being removed by sodium thiosulphate (p. 369). The paper is glazed by adding aluminium sulphate to the pulp, together with rosin soap, and gypsum as "filling." Insoluble aluminium resinate is formed which, on hot-rolling, becomes glossy. The paper then ceases to absorb ink.

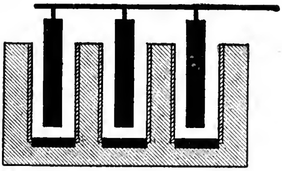


FIG. 403.—Calcium Carbide Furnace.

Calcium sulphide, CaS, is formed as *alkali-waste* in the Leblanc process, or by heating gypsum with charcoal: $CaSO_4 + 2C = CaS + 2CO_2$. It is insoluble in water, but dissolves when sulphuretted hydrogen is passed through the suspension, forming the **hydrosulphide,** $Ca(SH)_2$, which crystallises as $Ca(SH)_2,6H_2O$. The **polysulphides,** CaS_2 to CaS_5, or possibly CaS_7, appear to be contained in the reddish-yellow solution of sulphur in boiling milk of lime (*thion hudor*, p. 481). The crystals which separate from concentrated solutions are $CaS_4,3Ca(OH)_2,9H_2O$. The **thiosulphate,** $CaS_2O_3,6H_2O$, is formed by blowing air through a suspension of the sulphide, or by boiling the sulphite and sulphur with water. If the solution is precipitated with sodium carbonate, sodium thiosulphate is formed: $CaS_2O_3 + Na_2CO_3 = CaCO_3 + Na_2S_2O_3$. This can be crystallised by evaporation of the filtered solution.

Calcium carbide, CaC_2.—Calcium carbide, CaC_2, was obtained by Wöhler (1862) on heating carbon with an alloy of calcium and zinc. It is now manufactured on a large scale by Moissan's process. A mixture of 2 parts of coke and 3 parts of quicklime is heated to a very high temperature (2000°) in a closed electric furnace. The latter (Fig. 403) may consist of a rectangular tank of fireclay, divided into three compartments, lined with gas-carbon and having a graphite block in the base forming one electrode.

The other electrode consists of three vertical blocks of carbon, one in each compartment, suspended from chains and gradually lowered into the furnace as they become consumed. Arcs are struck between the base-plate and these electrodes, and at the high temperature reaction occurs, with the formation of fused carbide, which is tapped off, cooled, and broken into pieces in a jaw-crusher. The reaction : $CaO + 3C = CaC_2 + CO$, begins at 1620°. The commercial product is a greyish-black stony mass ; pure calcium carbide, formed by heating calcium hydride in acetylene, consists of colourless transparent crystals. Calcium carbide is decomposed by water, with production of acetylene (p. 678) : $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$; 1 kgm. of commercial carbide usually gives about 300 litres of gas. Commercial calcium carbide when heated in a stream of nitrogen, reacts with the formation of a mixture of **calcium cyanamide,** and graphite : $CaC_2 + N_2 = CaCN_2 + C$. About 10 per cent. of calcium chloride or fluoride is usually added as a flux. The product is used as a fertiliser in agriculture. If it is heated with water under pressure in autoclaves, with a little soda, steam being passed in, ammonia gas is produced : $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$. This is Frank and Caro's method for the **fixation of atmospheric nitrogen** (p. 544).

Calcium carbide is an energetic reducing agent. A mixture of powdered carbide with ferric oxide and ferric chloride burns violently when ignited with a taper, and fused metallic iron is produced.

Calcium nitrate, $Ca(NO_3)_2$.—This salt is present in the soil and serves as a plant food (p. 696). It is manufactured on a large scale by neutralising dilute nitric acid made by the arc process (p. 574) with limestone, and evaporating. It is also produced by passing oxides of nitrogen into milk of lime, or a suspension of calcium carbonate in water, until the nitrite in the mixture of nitrite and nitrate, first-produced, is decomposed, the oxides of nitrogen produced passing to more milk of lime (p. 576). The salt forms very deliquescent monoclinic crystals, $Ca(NO_3)_2,4H_2O$, soluble in alcohol. It is usually fused and cast into blocks for export. The fused salt is phosphorescent after exposure to light, and is sometimes called *Baldwin's phosphorus*, from its discoverer (1674).

Calcium phosphates.—The mineral phosphates have already been described (p. 608). Pure **calcium orthophosphate,** $Ca_3(PO_4)_2$, is formed as a white, flocculent precipitate on adding ordinary sodium phosphate to a solution of calcium chloride made alkaline with ammonia : $3CaCl_2 + 2Na_2HPO_4 + 2NH_4OH = Ca_3(PO_4)_2 + 4NaCl + 2NH_4Cl + 2H_2O$; or $3Ca^{\cdot\cdot} + 2HPO_4'' + 2OH' = Ca_3(PO_4)_2 + H_2O$. The precipitate is nearly insoluble in water, but is slowly decomposed on boiling into an insoluble basic and a soluble acid salt. It dissolves in water containing many salts, or dissolved carbon dioxide (which dissolves the calcium phosphate in the soil, and renders it capable of absorption by the roots of plants.) If a solution of calcium chloride is mixed with one of ordinary sodium phosphate, a white precipitate of **calcium hydrogen phosphate,** $CaHPO_4,2H_2O$, is formed. By dissolving either of the preceding salts in aqueous phosphoric acid, crystals of **tetra-hydrogen calcium phosphate,** $CaH_4(PO_4)_2$, are formed on spontaneous evaporation. They are decomposed by water : $CaH_4(PO_4)_2 = CaHPO_4 + H_3PO_4$. A mixture of $CaH_4(PO_4)_2$, and gypsum, known as **superphosphate of lime** (Fourcroy and Vauquelin, 1795), is prepared for use as a fertiliser, by macerating ground calcium phosphate in the form of bone-ash, phosphorites, etc., with two-thirds of its weight of sulphuric acid : $Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = CaH_4(PO_4)_2 + 2CaSO_4,2H_2O$. A mixture of chamber and Glover tower acids is used, and the phosphate is first dried and crushed. The reaction is carried out in a mixer, consisting of a horizontal cast-iron cylinder with revolving blades inside. The mixture issues in a nearly fluid state, and drops into pits or *dens*, which are half-filled, and then closed. The reaction takes place with rise of temperature, and gases (CO_2, SiF_4, HF, and HCl) escape through a vent to absorption towers. After a day or two, the superphosphate formed is removed by picks or mechanical elevators, powdered in a crusher, and carefully dried by hot air in long brickwork chambers. The total production of superphosphate is about 10 million tons per annum. On heating, the salt $CaH_4(PO_4)_2$ decomposes, with formation of insoluble **calcium pyro- and meta-phosphates:** $4CaH_4(PO_4)_2 = 3CaH_2P_2O_7 + Ca(PO_3)_2 + 5H_2O$.

Calcium oxalate, CaC_2O_4.—This salt is formed as a white precipitate insoluble in acetic acid but soluble in dilute hydrochloric acid, when ammonium oxalate solution is added to a solution of a calcium salt, preferably after adding ammonium chloride and ammonia. On gentle ignition it gives the carbonate : $CaC_2O_4 = CaCO_3 + CO$, which on heating to redness leaves the oxide, CaO. These reactions are used in the gravimetric estimation of calcium ; in the volumetric method the precipitate of oxalate is washed and dissolved in dilute hydrochloric acid. Sulphuric acid is added, and the oxalate titrated with standard permanganate : $2KMnO_4 + 5CaC_2O_4 + 8H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5CaSO_4 + 10CO_2 + 8H_2O$. Calcium oxalate occurs in small crystals (*raphides*) in some plants.

Glass.—The arts of making, working, and colouring glass appear to have been known to the Egyptians about 2000 B.C. From Egypt they spread to Rome, Constantinople, and Venice. An independent glass industry was established in Germany in the Middle Ages, and was introduced later to France and England.

Glass consists of a supercooled, very viscous, liquid solution of silicates ; if a long glass tube is supported at each end it bends permanently owing to its slight plasticity, but breaks with sudden shocks. Cobbler's wax shows similar properties. **Common glass**

contains calcium and sodium silicates, and has approximately the composition $Na_2O,CaO,6SiO_2$. Sodium silicate is soluble, but glass is practically insoluble in water, although boiling water removes some sodium silicate from it. Glass is made by fusing together silica (sand, crushed quartz, flints), calcium carbonate (limestone, marble, chalk), and either soda-ash (Na_2CO_3) or a mixture of salt-cake (Na_2SO_4) and carbon: $2Na_2SO_4 + C = 2Na_2O + CO_2 + 2SO_2$, in fireclay pots or tanks at about 1200°, and allowing the impurities to settle. On cooling to about 700°, the liquid becomes plastic, and can be blown or rolled. This gives ordinary **soda-glass.**

Bohemian, or **potash-glass,** contains potassium instead of sodium, and has a higher melting-point and greater resistance to reagents; for these reasons it is better adapted to making chemical apparatus. **Flint-glass** is soda or potash glass with lime partly replaced by lead oxide: litharge (PbO) is used in its manufacture. It has a high refractive index, and is used for optical purposes, but is very soft. Special varieties of glass (**Jena glasses**) invented by Schott and Abbe of Jena (who published their formulæ many years ago), contain boric, arsenic, and phosphoric anhydrides in place of some of the silica, and also potassium, zinc, aluminium, and barium oxides. They are made for various optical and chemical purposes. If good glass is heated to its softening point for a long time or inferior glass for a short time, some of the constituents crystallise, and the glass becomes opaque (*devitrification*). All varieties of glass require *annealing* before use: the objects are heated for a time and allowed to cool slowly. Toughened glass is obtained by cooling in oil. **Coloured glasses** are made by adding various metallic oxides to the fused glass; in the case of gold the colour only develops after reheating the glass for some time to increase the size of the colloidal particles which appear to be present:

Ruby: gold, or cuprous oxide.
Green: chromium oxide, or cupric oxide.
Yellow: antimony sulphide, silver borate, or selenium.
Violet: manganese dioxide.
Blue: cobalt oxide.
Opaque milky glass: tin oxide or calcium phosphate.
Fluorescent glass: uranium oxide.
Black glass: ferric oxide and cupric oxide.

Strontium, Sr = 86·93, and Barium, Ba = 136·28.

Strontium and barium minerals.—The mineral *heavy spar*, or *barytes* (Greek *baros* = heavy, from its high density, 4·5), is a very common vein stone in lead mines, where it is associated with galena, calcite, fluorite, and quartz, and is called *cawk* by the miners. In 1602, Vincentius Casciorolus, a shoemaker of Bologna, found that if barytes is ignited with charcoal, the residue is phosphorescent after exposure to light. Barium sulphide is formed by reduction of the sulphate (barytes): $BaSO_4 + 4C = BaS + 4CO$. In 1774, Scheele examined barytes, and concluded that it was the sulphate of a peculiar earth, called **baryta** by Lavoisier. Barium also occurs as the **carbonate**, $BaCO_3$, the mineral *witherite*, a gangue material in lead veins.

A peculiar mineral found in the lead mines of Strontian, in Argyleshire, was examined by Hope in 1791, and by Klaproth in 1793. They concluded that it was the carbonate of a new earth, different from lime and baryta, to which Klaproth gave the name of **strontia.** The mineral, called *strontianite,* is **strontium carbonate,** $SrCO_3$. **Strontium sulphate,** $SrSO_4$, occurs as the mineral *celestine,* so called from the pale blue colour of some specimens.

Strontium and barium salts.—If the *carbonates* are dissolved in hydrochloric acid, the iron in the solutions oxidised with chlorine water, precipitated by boiling with a little of the strontium or barium carbonates obtained by adding sodium carbonate to a portion of the solution, and the filtered liquid evaporated, crystals of **strontium chloride,** $SrCl_2,6H_2O$, or **barium chloride,** $BaCl_2,2H_2O$, are formed. The former are efflorescent, but the latter are unchanged in the air. Strontium chloride is soluble in alcohol, whilst barium chloride is insoluble. This property may be used to separate calcium and strontium (chlorides soluble in alcohol) from barium (chloride insoluble).

By carrying out the above operation with dilute nitric, instead of with dilute hydrochloric, acid, **strontium nitrate,** $Sr(NO_3)_2$, and **barium nitrate,** $Ba(NO_3)_2$, are formed. These salts are used in pyrotechny to produce *crimson* and *green fire,* respectively, by mixing them with sulphur and charcoal. They are insoluble in alcohol (calcium nitrate is soluble).

To prepare soluble salts from the natural **mineral sulphates,** which are sparingly ($SrSO_4$), or not at all ($BaSO_4$), soluble in acids, they may be fused with sodium carbonate, when the carbonates are produced, and may be separated from the alkali sulphate by boiling the mass with water and washing: $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$. In another process the minerals are strongly heated with carbon, when the sulphides are formed: $BaSO_4 + 4C = BaS + 4CO$. The carbonates or sulphides may then be dissolved in acids, and the salts crystallised.

Strontium carbonate is decomposed at a higher temperature than calcium carbonate, whilst **barium carbonate** is stable at a bright red heat. If, however, the carbonates are mixed with charcoal, heated to redness, and exposed to a current of steam, the **hydroxides** are formed: $BaCO_3 + C + H_2O = Ba(OH)_2 + 2CO$. The **oxides** are best prepared by heating the nitrates. They are white, amorphous substances resembling quicklime, and combine with water to form hydroxides with evolution of heat. **Strontium hydroxide,** $Sr(OH)_2,8H_2O$, is crystalline, and dissolves fairly readily in hot water; on heating to redness, it loses water and leaves **strontia,** SrO. **Barium hydroxide** also forms a crystalline hydrate, $Ba(OH)_2,8H_2O$, which dissolves readily in hot water. On exposure to air free from carbon dioxide the crystals effloresce, forming $Ba(OH)_2,H_2O$. Barium hydroxide fuses on heating strongly, but does not lose water even at a very high temperature; **baryta,** BaO, is prepared by igniting the nitrate. A solution of barium hydroxide in water is called **baryta-water,** and gives a white precipitate of the carbonate, $BaCO_3$, with carbon dioxide.

Baryta in solution is a strong base, and is often used in volumetric analysis instead of caustic soda, since any carbonate formed by exposure to air is precipitated and does not remain in solution to interfere with the colour-changes of indicators. Barium salts are poisonous.

Baryta and strontia, as well as lime, form sparingly soluble compounds, called **saccharates**, with cane-sugar. These are used in separating the sugar from the molasses residues of beet-sugar (which are not palatable); since barium compounds are poisonous, the strontium or calcium compounds are used in practice: $C_{12}H_{22}O_{11},2SrO$; $C_{12}H_{22}O_{11},3CaO$. The precipitates, after washing, are suspended in water and decomposed by a current of carbon dioxide. The carbonate is precipitated, pure sugar remains in solution, and may be crystallised.

Barium peroxide, BaO_2, is obtained by passing oxygen or air over baryta heated to dull redness: $2BaO + O_2 \rightleftharpoons 2BaO_2$. The dissociation pressures at different temperatures are:

555°	650°	720°	790°	795°
25	65	210	670	760 mm.

Strontium peroxide, SrO_2, is formed from the monoxide and oxygen at a dull red heat under a pressure of 125 kgm./sq.cm., and is similar to barium peroxide. (Calcium peroxide has not yet been obtained directly.) The hydrates of barium and strontium peroxides $BaO_2,8H_2O$ and $SrO_2,8H_2O$, are obtained as crystalline precipitates, by adding hydrogen peroxide to cold saturated solutions of barium and strontium hydroxides. On gently heating, the hydrates lose water and form BaO_2 and SrO_2. By precipitating a concentrated solution of the hydroxide above 40°, anhydrous SrO_2 is formed; below 40° the compounds BaO_2,H_2O_2 and $BaO_2,2H_2O_2$ are formed with excess of hydrogen peroxide and baryta-water.

Metallic strontium and **barium** are obtained by the electrolysis of the fused chlorides, preferably mixed with potassium chloride, or by heating the oxides with aluminium powder *in vacuo*. They are silver-white. Strontium (sp. gr. 2·5) melts at 900°, barium (sp. gr. 3·6) at 850°. Barium is also obtained by heating the oxide with silicon in an evacuated steel tube: $3BaO + Si = BaSiO_3 + 2Ba$. The metal distils off.

Barium sulphate, $BaSO_4$, is formed as a fine white precipitate insoluble in acids (except hot concentrated sulphuric acid, from which crystals of the **acid sulphate**, $Ba(HSO_4)_2$, separate on cooling, or in hot very concentrated hydrochloric acid), by adding sulphuric acid or a sulphate to a barium salt. It is used as a pigment (*permanent white*), but has a poor covering power. *Lithopone* is a mixture of $BaSO_4$ and zinc sulphide made by precipitation: $BaS + ZnSO_4 = BaSO_4 + ZnS$. It has a better covering power even than white lead (p. 928), and does not darken on exposure to sulphuretted hydrogen.

EXERCISES ON CHAPTER XL

1. In what forms does calcium carbonate occur? How is quicklime manufactured from limestone?
2. Starting from quicklime, how would you prepare calcium peroxide, chloride, sulphide, and nitrate?
3. Describe the general properties of the alkaline-earth elements. Discuss the position of magnesium in the group.
4. How are barium and strontium salts obtained from the minerals?
5. Describe the preparation of: (*a*) metallic calcium, (*b*) barium fluoride, (*c*) strontium nitrate from celestine. What are the properties of these substances?
6. How are mortar, cement, and glass made? What is known of the composition of these materials?
7. Describe the manufacture of calcium carbide. What important substances are prepared from it?
8. What is "superphosphate of lime"? How is it manufactured?

CHAPTER XLI

THE METALS OF THE ZINC GROUP

Beryllium, Be = 9·0.—Vauquelin, in 1798, found that the mineral *beryl* (Fig. 404) contains a peculiar earth, which he called **glucina,** differing from lime and alumina by forming a soluble sulphate which does not produce alums. The Peruvian *emerald* (*cf.* p. 894) is a transparent variety of beryl, coloured green by oxide of chromium. The formula of beryl is $3BeO,Al_2O_3,6SiO_2$. To prepare beryllium salts from beryl, it is fused with potassium carbonate, the melt evaporated with sulphuric acid, and digested with water. Silica is filtered off, and on cooling the evaporated filtrate, nearly all the aluminium separates in the form of potash alum. The mother liquor is then poured into a concentrated solution of ammonium carbonate. **Beryllium hydroxide** and **carbonate,** $Be(OH)_2$ and $BeCO_3$, are soluble in ammonium carbonate, whilst ferric hydroxide and alumina are precipitated. The filtrate on boiling deposits a basic beryllium carbonate. If this is ignited, **beryllium oxide,** or **beryllia,** BeO, remains as a white powder soluble in hot concentrated sulphuric acid; the solution on cooling deposits crystals of **beryllium sulphate,** $BeSO_4,4H_2O$, possessing a sweet taste (hence the name *glucinum*, often given to the element). The sulphate does not form mixed crystals with $CuSO_4$, $FeSO_4$, etc., and thus differs from $ZnSO_4$ and $MgSO_4$. By passing chlorine over a heated mixture of the oxide and carbon, the **chloride,** $BeCl_2$, sublimes in white crystals which fume in moist air. The vapour density of the chloride at 520° corresponds with the formula $BeCl_2$ (p. 469). Metallic **beryllium** is obtained by the electrolysis of a fused mixture of the chloride with sodium and ammonium chlorides, or of the fluoride with sodium fluoride in a nickel crucible with a carbon anode. It is a hard, white metal, sp. gr. 1·842, m.-pt. 1278°, which burns brilliantly in the air when heated in the form of powder, but does not decompose steam even at a red heat.

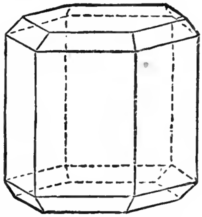


FIG. 404.—Crystal of Beryl.

Beryllium hydroxide, $Be(OH)_2$, is soluble in alkalies, but is reprecipitated on diluting the solution. It is readily soluble in ammonium carbonate. By these reactions it is distinguished from alumina, which it otherwise closely resembles.

MAGNESIUM. $Mg = 24{\cdot}13$.

Magnesium.—In 1695, Nehemiah Grew obtained from the water of a mineral spring at Epsom a peculiar salt which was called **Epsom salts**. The salt was afterwards found in other mineral springs, in the mother liquors from the preparation of common salt from sea-water, and in saltpetre mother liquors. Epsom salt is **magnesium sulphate**, $MgSO_4,7H_2O$; **magnesium chloride**, $MgCl_2$, is contained in sea-water. By precipitating solutions of these salts with potassium or sodium carbonate, *magnesia alba*, which like Epsom salt is used medicinally, is obtained. Black, in 1755, showed that magnesia alba is a compound of fixed air, or carbon dioxide, with *calcined magnesia*, or **magnesium oxide**, MgO, left after ignition of magnesia alba. Metallic magnesium was obtained in an impure state by Davy.

Magnesium is widely distributed, occurring in the forms of *magnesite*, $MgCO_3$; *dolomite*, $MgCO_3,CaCO_3$; *kieserite*, $MgSO_4,H_2O$; *kainite*, $MgSO_4,K_2SO_4,MgCl_2,6H_2O$; and *carnallite*, $KCl,MgCl_2,6H_2O$. It is also contained in *spinel*, MgO,Al_2O_3, and is an important constituent of rocks: *olivine*, Mg_2SiO_4; *talc*, $Mg_3H_2(SiO_3)_4$; *asbestos*, $CaMg_3(SiO_3)_4$; *meerschaum*, $H_2Mg_2(SiO_3)_3,H_2O$, *augite*, *olivine*, and *serpentine* (p. 746) are common rock-forming minerals. All plant- and animal-tissues contain magnesium; it appears to be an essential constituent of *chlorophyll*, the green colouring-matter of plants (p. 694).

Magnesium salts considerably in excess of demand are obtained as by-products at Stassfurt (p. 790).

Magnesium sulphate, $MgSO_4$.—Magnesium sulphate is prepared from *magnesite*, $MgCO_3$, or *dolomite*, $MgCO_3,CaCO_3$. Magnesite occurs in large masses in various localities, *e.g.*, in Greece. If magnesite or dolomite is boiled with dilute sulphuric acid, calcium carbonate is converted into the sparingly soluble gypsum, and magnesium sulphate goes into solution. Iron is separated by boiling with a little precipitated magnesium carbonate, and the filtrate on evaporation and cooling yields crystals of **magnesium sulphate,** $MgSO_4,7H_2O$ (*Epsom salts*) (Fig. 405). These are also formed by dissolving kieserite in boiling water (it is practically insoluble in *cold* water), and crystallising. Magnesium sulphate is used as a purgative, as a dressing for cotton goods, and in dyeing with aniline colours.

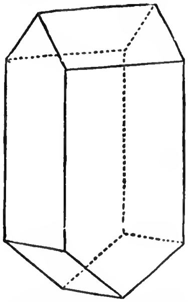


FIG. 405.—Epsom Salt Crystal.

Several hydrates of $MgSO_4$ are known, *e.g.*, with $7H_2O$, $6H_2O$, and H_2O; at 200°, the anhydrous sulphate is formed from the hydrates. The hydrate $MgSO_4,7H_2O$ is formed from supersaturated solutions on cooling; it is isomorphous with $ZnSO_4,7H_2O$. Double salts with alkali-metals are readily formed, *e.g.*, $MgSO_4,K_2SO_4,6H_2O$ is *schönite*, a Stassfurt mineral. A solution of the anhydrous sulphate in concentrated sulphuric acid deposits crystals of $MgSO_4,H_2O$.

The **double salts** in solution are completely decomposed into the single salts, as is shown by the magnitude of the depression of freezing point. They are in this way distinguished from **complex salts,** such as $K_4Fe(CN)_6$, which retain their constitution in solution, and ionise accordingly: $K_4Fe(CN)_6 \rightleftharpoons 4K^{\cdot} + Fe(CN)_6''''$. The solution then does not exhibit the reactions of the components of the complex ion (*e.g.*, $Fe^{\cdot\cdot}$, and CN'). Isomorphous mixtures, or **mixed crystals,** *e.g.*, a mixture of $FeSO_4,7H_2O$ and $MgSO_4,7H_2O$, differ from double salts by having a variable composition. They may be represented by such formulæ as $(Fe,Mg)SO_4,7H_2O$ (*cf.* p. 446).

Magnesium chloride, $MgCl_2$.—*Carnallite*, $KCl,MgCl_2,6H_2O$, occurs in large quantities in the Stassfurt deposits (p. 790). It fuses at 176°, undergoing decomposition with deposition of practically all the potassium chloride. Fused **magnesium chloride**, $MgCl_2,6H_2O$, remains. On cooling this the rest of the potassium deposits as carnallite, and the fused residue of magnesium chloride solidifies to a crystalline mass of $MgCl_2,6H_2O$. The crystals are very deliquescent, and are used in lubricating cotton thread in spinning. Magnesium chloride forms several hydrates, viz., with $12H_2O$, $8H_2O$ (α and β), $6H_2O$, $4H_2O$, and $2H_2O$. If the crystalline hydrates are heated above 186° they undergo hydrolysis: hydrochloric acid and steam are evolved, and magnesium oxide is left: $MgCl_2 + H_2O = MgO + 2HCl$. **Anhydrous magnesium chloride,** $MgCl_2$, is prepared by heating the hexahydrate in a vacuum at 175°, or in a current of hydrogen chloride. Another method is to add ammonium chloride to the solution, evaporate, and heat in a covered crucible. The double salt, $MgCl_2,NH_4Cl,6H_2O$, loses water, and the residual $MgCl_2,NH_4Cl$ on further ignition evolves a mixture of hydrogen chloride and ammonia, leaving fused anhydrous magnesium chloride, $MgCl_2$.

The hydrolysis is prevented by the production of the stable compound $MgCl_2,NH_4Cl$, from which the water may be completely removed at a temperature below that at which decomposition occurs. **Magnesium bromide,** $MgBr_2,8H_2O$, and **iodide,** $MgI_2,8H_2O$, occur in some mineral springs, and are prepared in the same way as the chloride, by dissolving magnesium oxide or carbonate in the acids.

If a concentrated solution of magnesium chloride is mixed with magnesium oxide, the paste solidifies to a hard, white mass of the **oxychloride**, Mg(OH)Cl. This is used as a dental stopping, and as a finish for plaster, since it takes a fine polish.

Magnesium.—Metallic **magnesium** is prepared by the electrolysis of fused carnallite, which loses water and fuses to a clear liquid at 700°. Calcium fluoride is also added. The cathode is the iron crucible, the anode is of carbon. The chlorine is led off, and the metal floats to the surface, being protected by a current of coal gas. The semi-fused metal is pressed into wire, which is then rolled into *ribbon*. It appears to be prepared in England by Vickers by the old expensive process of reducing the fused double chloride of magnesium and sodium with metallic sodium. Magnesium may also be prepared by the electrolysis of a solution of magnesium ammonium sulphate at 70–100°. Metallic magnesium in the form of ribbon burns when heated in air with an intense white light, producing the oxide, MgO, and a little **nitride**, Mg_3N_2. The residue, when moistened with water, therefore gives off a little ammonia. Magnesium powder mixed with powdered potassium chlorate or barium peroxide burns explosively when lighted, producing a blinding white flash. The mixture is used in photography, and for signalling and star-shells. A mixture of magnesium and dry amorphous silica is also used. The metal is stable in dry air, but soon becomes covered with oxide in moist air: the alloys with lead, containing Mg_2Pb, rapidly oxidise in air. Magnesium melts at 651°, and boils at 1100°. It is very light (sp. gr. 1·75). Fine crystals are formed by subliming the metal in an evacuated tube at about 550°. The metal dissolves readily in dilute acids, but not in alkalies. Magnesium powder decomposes water (p. 182). A colloidal solution in ether can be prepared by Bredig's method.

Magnesium combines directly with nitrogen on heating, forming a **nitride**, Mg_3N_2, a greenish-yellow, amorphous mass, decomposed by water: $Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$. A **sulphide**, MgS, two **carbides**, MgC_2 and MgC_3, and two **silicides**, Mg_2Si and MgSi, are formed by direct combination. The sulphide is at once hydrolysed by water, although a solution, probably containing the **hydrosulphide**, $Mg(HS)_2$, is formed by passing sulphuretted hydrogen through the oxide suspended in water. It decomposes on warming, evolving *pure* hydrogen sulphide. The **phosphide**, Mg_3P_2, and **arsenide**, Mg_3As_2, are formed by direct combination and are decomposed by water.

Magnesia, MgO.—By precipitating a solution of magnesium sulphate or chloride with caustic soda, and drying at 100°, the sparingly soluble **hydroxide**, $Mg(OH)_2$, is formed, insoluble in excess of alkali. This occurs crystalline as the mineral *brucite*. On heating, the hydroxide loses water and forms the **oxide**, MgO, which occurs in octahedral crystals as *periclase*. Magnesium oxide is usually prepared by heating the basic carbonate (*q.v.*), or native magnesite, and is known as *calcined magnesia.* Two varieties are formed, from the light and heavy carbonates respectively, the specific gravities of which are in the ratio 1 : 3·5. The oxide slowly combines with water, forming the hydroxide, and when moist turns red litmus paper blue. It fuses at about 2250°, and is reduced by carbon in the electric furnace, forming magnesium carbide. A crystalline form is produced on heating the powder strongly in a current of hydrogen chloride.

Magnesia, prepared by the calcination of native magnesite, is used in the manufacture of *refractory bricks* for electric furnace-linings. These are *basic*, and resist the action of basic slags containing lime. *Acidic* linings are composed of ganister (largely silica), and *neutral* linings of chromite or chrome-ironstone (p. 947). Bricks containing 90 parts of MgO, 5FeO, and 5 of silica, chalk, and clay, sinter above 1400°, but do not fuse below 2000°.

The solubility of magnesium hydroxide (1 part in 55,000 of water) is reduced by the addition of potash or soda, in accordance with the equation $Mg(OH)_2 \rightleftharpoons Mg^{\cdot\cdot} + 2OH'$, but is increased by the addition of ammonia, and especially of ammonium chloride. This reaction is applied in qualitative analysis, where magnesium is kept in solution by ammonium chloride whilst the metals of the groups III, IV, and V are precipitated by NH_4OH, NH_4HS, and $(NH_4)_2CO_3$, respectively.

The solubility of magnesium hydroxide in ammonium salts is due to the feeble ionisation of ammonium hydroxide, NH_4OH. If an ammonium salt is brought in contact with $Mg(OH)_2$, the OH' ions of the latter are withdrawn from the solution to form practically un-ionised NH_4OH, the ionisation of which is still further reduced by the excess of $NH_4^{\cdot}$ ions of the NH_4Cl. More $Mg(OH)_2$ therefore dissolves and dissociates, to provide a further supply of OH' ions, and the process goes on until the solubility product $[Mg^{\cdot\cdot}] \times [OH']^2$ is reached, or if this cannot be attained, until all the $Mg(OH)_2$ is dissolved.

A **peroxide,** probably MgO_2, is obtained in an impure state by precipitating a solution of the sulphate, mixed with hydrogen peroxide, with caustic soda. After drying, it contains about 8 per cent. of available oxygen, and is used as an antiseptic in tooth-pastes, etc.

Magnesium carbonates.—The **normal carbonate,** $MgCO_3$, occurs native as *magnesite.* The precipitates formed by adding carbonates to solutions of magnesium salts are always **basic carbonates.** From solutions at the ordinary temperature, the precipitate is a light loose powder—*magnesia alba levis*, of the composition $4MgCO_3 + Mg(OH)_2 + 5H_2O$. From a boiling solution, a denser crystalline precipitate, $MgCO_3 + Mg(OH)_2 + 4H_2O$, *magnesia alba ponderosa*, is thrown down. Both are used in medicine. If the basic salts are suspended in water, and a current of carbon dioxide is passed through, they dissolve, producing a *bicarbonate*. The solution containing 2·65 gm. of $Mg(HCO_3)_2$ per 100 c.c., is known as *fluid magnesia*. If the solution is heated to 50°, crystals of **magnesium carbonate**, $MgCO_3,3H_2O$, separate.

Magnesium phosphate, $Mg_3(PO_4)_2$.—This compound occurs in bones and in plant-tissues, and is precipitated from solutions of magnesium salts by trisodium phosphate, Na_3PO_4. Ordinary sodium phosphate, Na_2HPO_4, precipitates **magnesium hydrogen phosphate**, $MgHPO_4$, soluble in 322 parts of cold water. On heating the solution, the normal salt, $Mg_3(PO_4)_2$, is precipitated, and an acid salt, supposed to be $MgH_4(PO_4)_2$, remains dissolved. If a solution of a magnesium salt is mixed with solutions of ammonium chloride and ammonia, and a phosphate added, a crystalline precipitate is deposited, slowly from dilute solutions, but more rapidly on stirring or scratching the sides of the beaker with a glass rod. This consists of **magnesium ammonium phosphate**, $Mg(NH_4)PO_4,6H_2O$. This substance is present in some urinary calculi; it is sparingly soluble in water (1 part in 15,000), and less so in dilute ammonia (1 part in 44,000); its formation is a delicate test for a phosphate (p. 632), or magnesium.* On ignition, it is converted into the **pyrophosphate**, $Mg_2P_2O_7$, in which form magnesium is estimated in gravimetric analysis: $2Mg(NH_4)PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$.

Magnesium is separated from the alkalies by adding baryta-water, when $Mg(OH)_2$ is precipitated. The excess of baryta is precipitated from the filtrate by saturation with carbon dioxide, when $BaCO_3$ is formed, leaving the alkali carbonates in solution. The precipitate of $Mg(OH)_2$ is washed, dissolved in dilute hydrochloric acid, and precipitated as $MgNH_4PO_4$.

The **atomic weight** of magnesium was determined by the analysis of the anhydrous chloride, prepared by heating $MgCl_2,NH_4Cl$ in a current of HCl gas. It is 24·13 (H = 1).

ZINC. Zn = 64·85.

Zinc minerals.—The ancients prepared *orichalcum*, or *brass*, an alloy of zinc and copper, by heating copper with an ore known as *cadmia* and charcoal. Cadmia, which was called *tutia*, or *tutty*, by the alchemists, was probably zinc carbonate, $ZnCO_3$. Since the copper was turned a golden-yellow colour by this process, tutia

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* *Magnesia mixture*, for the precipitation of phosphates, is prepared by dissolving 50 gm. of $MgCl_2,6H_2O$ and 75 gm. of NH_4Cl in 1 litre of 4 per cent. ammonia solution.

was looked upon as an approach to the Philosopher's Stone. Thus, Geber says: copper "agrees very well with *Tutia*, which citrinizeth it with good yellowness; and hence you may reap profit. Therefore take it, before all other Imperfect *Bodies*, in the *Lesser* and *Middle Work*, but not in the *Greater*."

The metal itself is first mentioned by Paracelsus, who refers to it as *zinken*—a "semi-metal" or "a spurious son of copper" (probably on account of its brittle character). The name *spelter* for the metal is used by Boyle, but was also applied to bismuth, with which zinc was confused. Libavius describes the metal, which he says was brought from the East Indies. The real nature of brass was not clear until Kunckel observed that: "calamine allows its mercurial [*i.e.*, metallic] part to pass into the copper and form brass." Zinc was identified as the metal from blende (ZnS) by Homberg in 1695; the extraction of the metal from calamine was effected by Lawson early in the following century.

Zinc occurs chiefly as *blende*, ZnS, usually coloured yellow or brown by iron ("black-jack" of the miners), and possessing a characteristic resinous lustre. It is found in England, in many parts of Europe and America, and in New South Wales. The carbonate occurs as *calamine*, or *smithsonite*, $ZnCO_3$, in Belgium, Germany, and America. *Electric calamine* is a silicate, Zn_2SiO_4,H_2O. The oxide, *zincite*, ZnO, is a rare ore, but the ferrite, $Zn(FeO_2)_2$, or ZnO,Fe_2O_3, forms the very important *franklinite*, or *red zinc ore*, deposit of Franklin Furnace, New Jersey. The New South Wales ore contains galena, and is first "concentrated" by the **flotation process** (p. 10). Certain varieties of pyrites, *e.g.*, Westphalian, contain zinc sulphide. Traces of zinc occur, as an organic compound, in animal cells, and especially in snake venom (0·11–0·50 per cent.).

Metallurgy of zinc.—The extraction of zinc from its ores was in operation on an extensive scale at Bristol in 1743, the roasted ore (ZnO) being distilled with carbon at a high temperature in a crucible the bottom of which was perforated and fitted with a piece of iron pipe passing above the surface of the mixture inside. Zinc is a volatile metal (b.-pt. 918°), and distilled off, the vapour condensing in the lower part of the tube to liquid metal, which ran into water. This process is no longer used. In 1807 zinc smelting was begun at Liége, in Belgium, and later on spread to Silesia. These two processes are still in use, and are called the **Belgian process,** and the **Silesian process,** respectively. In America, franklinite ore is used; in Europe, blende.

The ore is first roasted, and the sulphur dioxide produced from blende may be utilised in the manufacture of sulphuric acid. External heating has to be applied, the ore being raked in a series of muffles, through which air circulates. Care must be taken that only the oxide is produced: $2ZnS + 3O_2 = 2ZnO + 2SO_2$, since the sulphate, $ZnSO_4$, if formed, is very stable, and would, in the subsequent reduction, again give sulphide, leading to considerable loss. The roasted ore is next mixed with half its weight of powdered coal and charged into fireclay retorts, which are strongly heated. Zinc distils off: $ZnO + C = Zn + CO$. The reduction begins at 800°, and increases rapidly with rise of temperature. The **Belgian retorts** consist of fireclay tubes, closed at one end and set in a furnace, sloping towards the open end (Fig. 406). An iron tube is luted into the open end with clay and serves to condense the zinc. The **Silesian retorts** are fireclay muffles (Fig. 407), to which a fireclay elbow and an iron condenser tube are luted; they are heated in a furnace. The newer furnaces employ three rows of muffles, one above the other, the lower row being supported along their length on the hearth, and the two upper rows only at the ends. They are fired with gas. In all cases 10–25 per cent. of the zinc is lost. The production in 1909 was 800,000 tons.

The ore is also smelted to a limited extent in the **electric furnace,** either of the arc or resistance type, but a considerable proportion of the metal is then obtained in the form of a powder mixed with oxide, known as **zinc dust,** which is also produced, to a less extent, in the coal-fired furnaces.

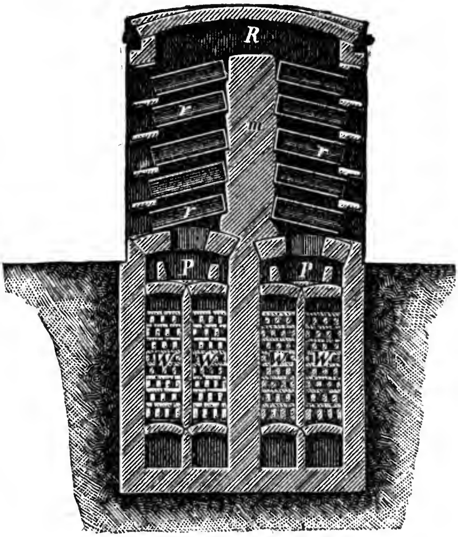


FIG. 406.—Belgian Zinc Furnace.

Commercial zinc, called *spelter*, contains about 97–98 per cent. of zinc, 1–3 per cent. of lead, and some arsenic. It is **refined** by electrolysis in an acid solution of zinc sulphate with a high current density (Pring and Tainton). This metal contains 99·9 per cent. of zinc. Zinc is also leached from burnt pyrites containing it, with ferric sulphate solution, and deposited electrolytically. The impure metal dissolves readily in dilute acid, whereas some varieties of the pure metal dissolve slowly unless a few drops of copper sulphate or platinic chloride solution are added. Metallic copper, or platinum is precipitated on the zinc, and forms a galvanic couple, from the insoluble part of which hydrogen is readily evolved. For use in the laboratory the metal is usually **granulated** by melting in a clay crucible and pouring into a bucket of water. **Zinc foil,** or *sheet,* is prepared by heating the metal to 100–150°, when it becomes soft, and rolling it.

Metallic zinc.—Zinc has a bluish-white colour, melts at 419°, and boils at 918°. Its vapour density corresponds with the formula Zn. The metal is hard and moderately brittle; it softens at 100–150°, but becomes very brittle at 205°, and can then be powdered in a mortar. It readily burns in air when the turnings are heated in a flame, or the metal is heated strongly in a crucible, producing a white cloud of oxide, which settles out in the form of woolly flocks. These were called "Philosophers' wool" by the alchemists, or, in Latin, *nix alba* (white snow). This name was rendered as "Weisses Nichts" into German, and thence, by Teutonic erudition, *nihilum album.* The metal oxidises in moist air, forming the basic carbonate, and is attacked and dissolved by soft water, especially that containing peat acids. The zinco-solvency of water is reduced by allowing it to stand over limestone.

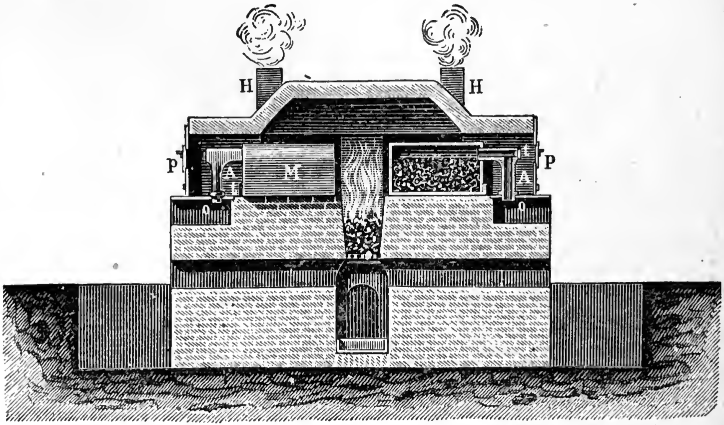


FIG. 407.—Silesian Zinc Furnace.

Zinc and copper are the constituents of the valuable alloy *brass.* Zinc is miscible in a state of fusion with tin, copper, and antimony, but only partly dissolves in lead and bismuth (*cf.* p. 820).

Zinc is more resistant to moist air than, and is used as a protection for, iron. The iron sheets or wire are cleaned by a sand-blast, and dipped into molten zinc, when an adherent coating of the latter is formed. This process is known as **galvanising,** and the product as **galvanised iron.** Iron articles may also be coated with zinc by heating them in zinc dust; this is known as **sherardising.** The zinc dissolves before iron in presence of oxygen and moisture, since it is more electropositive than the other metal. The metal is also used for the positive electrodes of voltaic cells (p. 881).

Zinc dissolves in dilute acids, evolving hydrogen (except with nitric acid), and producing **zinc salts** (p. 185), containing the **zinc ion,** $Zn^{\cdot\cdot}$. It also dissolves readily in hot solutions of caustic potash and soda, evolving hydrogen, and forming solutions of **zincates:** $Zn + 2KOH = K_2ZnO_2 + H_2$.

Zinc oxide, ZnO.—**Zinc oxide,** ZnO, is produced by the combustion of the metal; when so prepared it is called *zinc white* and is used as a pigment. It is prepared for pharmaceutical purposes by precipitating a solution of zinc sulphate with sodium carbonate, and igniting the basic carbonate. It is a white powder which becomes sulphur-yellow on heating, the colour disappearing on cooling. Zinc oxide sublimes readily at 1400°. On exposure to air it takes up a little water. Zinc oxide dissolves readily in acids, producing zinc salts, and in alkalies, forming zincates, *e.g.*, $KHZnO_2$, and $NaHZnO_2,3H_2O$, which can be obtained in the solid state.

Zinc hydroxide, $Zn(OH)_2$, is formed as a white, flocculent precipitate on adding caustic potash or soda to a solution of a zinc salt. It can be dried at 85°, but loses water at higher temperatures. Zinc hydroxide dissolves in 190,000 parts of water. The precipitate is readily soluble in excess of the alkali, producing a solution containing colloidal zinc hydroxide and a little zincate. Zinc hydroxide is therefore feebly acidic as well as basic; it is an **amphoteric substance.** Ammonia also dissolves it, forming a complex hydroxide: $Zn(NH_3)_4(OH)_2 \rightleftharpoons Zn(NH_3)_4^{\cdot\cdot} + 2OH'$.

By the action of 30 per cent. hydrogen peroxide on zinc oxide at $-10°$, a white, or yellow, powder is obtained, which is believed to be a hydrated **peroxide,** ZnO_2,Aq. By the action of 30 per cent. H_2O_2 on a solution of zinc oxide in caustic soda (sodium zincate), a white precipitate of the formula ZnO_2,H_2O, or ZnO,H_2O_2, is formed. Precipitates obtained by adding zinc sulphate to solutions of Na_2O_2 are probably mixtures of zinc hydroxide and peroxide.

Zinc oxide is used as an absorbent in surgical dressing, as a "filling" for rubber, and in the preparation of *Rinman's green.* The latter is obtained by heating zinc oxide with a solution of cobalt nitrate, and is either cobalt zincate, $CoZnO_2$, or a solid solution of cobalt oxide in zinc oxide. The formation of this green substance is the basis of the blowpipe test for zinc.

Zinc chloride, $ZnCl_2$.—Anhydrous **zinc chloride** (b.-pt. 730°) is formed by passing hydrogen chloride over heated zinc, or by distilling the metal with mercuric chloride: $HgCl_2 + Zn = Hg + ZnCl_2$. It is formed in solution by dissolving zinc or its oxide in concentrated hydrochloric acid (Glauber, 1648—*oil of calamine*). On evaporation, a syrupy liquid is obtained; if a little concentrated hydrochloric acid is added to this, small, deliquescent crystals, $ZnCl_2,H_2O$, separate. If, however, the aqueous solution is evaporated to dryness, the **oxychlorides** $Zn(OH)Cl$ and Zn_2OCl_2, are formed. An oxychloride is also produced by mixing the syrupy solution of the chloride with zinc oxide and finely powdered glass; the whole sets rapidly to a very hard mass, used as a dental stopping. The concentrated solution of zinc chloride is used for impregnating timber to prevent its destruction by micro-organisms ("dry rot"), and as a caustic (it dissolves proteins). In timber-preserving, zinc chloride is being replaced by fluorides. By evaporation in a current of hydrochloric acid gas the fused salt is obtained, which may be cast into sticks.

A solution of zinc chloride prepared by adding zinc to commercial hydrochloric acid (spirits of salt) is used under the name of "killed spirits" as a flux in soldering. On heating, it liberates hydrochloric acid, which dissolves metallic oxides and keeps the metal surface clean. Hot zinc chloride solution dissolves cellulose, forming a colloidal solution. If this is squirted into alcohol, a thread of amorphous cellulose is formed, which is carbonised by heating, and forms the carbon filament of electric lamps. Zinc chloride is used, like magnesium chloride, for "filling" (*i.e.*, weighting and adulterating) cotton goods. The double salts, $ZnCl_2,2NH_4Cl$ and $ZnCl_2,3NH_4Cl$, are formed as crystals in Leclanché batteries, and zinc chloride absorbs ammonia gas. The double salts are hydrolysed by water, with deposition of white oxychlorides, which dissolve in dilute hydrochloric acid.

The **bromide** and **iodide,** ZnX_2, are formed from the elements in presence of water.

Zinc sulphate, $ZnSO_4$.—**Zinc sulphate,** $ZnSO_4,7H_2O$, isomorphous with Epsom salts, is known as *white vitriol.* It was described by Basil Valentine (p. 29), and was produced by lixiviating roasted blende. Its composition was correctly given by Neumann (1735). The substance is the commonest salt of zinc, and is prepared by dissolving the metal, oxide, or carbonate in dilute sulphuric acid and evaporating (p. 185). It forms several hydrates; on heating $ZnSO_4,7H_2O$ to 100°, $ZnSO_4,H_2O$ is left, which loses water only at a dull red heat. When strongly heated, sulphur trioxide is evolved and zinc oxide remains. Double salts, *e.g.*, $K_2SO_4,ZnSO_4,6H_2O$, are easily prepared. A solution of white vitriol ($\frac{1}{8}$ per cent. $ZnSO_4$) is used as an eye lotion, and the sulphate is used in the manufacture of lithopone (p. 853).

Zinc sulphide, ZnS.—**Zinc sulphide,** ZnS, occurs as *blende,* which is phosphorescent on heating, and exhibits luminous effects on exposure to α-rays and X-rays. An artificial phosphorescent sulphide (**Sidot's blende**) is formed on heating the precipitated sulphide to whiteness in a covered crucible; it is used in making phosphorescent screens for *X*-ray and radioactivity work. Perfectly pure zinc sulphide is not phosphorescent; the property is conferred by traces of sulphides of heavy metals (bismuth, copper, manganese). Zinc sulphide is obtained as a white precipitate on adding ammonium sulphide to a solution of a zinc salt; it dissolves in all dilute mineral acids, but not in acetic acid (*cf.* MnS). If sulphuretted hydrogen is passed through a solution of zinc sulphate, zinc sulphide is at first precipitated, but owing to the acid formed the precipitation soon ceases: $ZnS + 2H^{\cdot} \rightleftharpoons Zn^{\cdot\cdot} + H_2S$. If sodium acetate is added to the solution, the concentration of hydrogen ions is kept low by the formation of the very weak acetic acid: $C_2H_3O_2' + H^{\cdot} \rightleftharpoons C_2H_4O_2$. If nickel and cobalt are present, they are precipitated only after all the zinc has been thrown down.

Zinc carbonate, $ZnCO_3$.—Sodium carbonate precipitates a **basic carbonate** from a solution of a zinc salt, the composition depending on the concentrations and temperature. A solution of a bicarbonate, *e.g.*, $NaHCO_3$, however, gives a white precipitate of **zinc carbonate,** $ZnCO_3$. This is soluble in a concentrated solution of potassium carbonate, but is precipitated on dilution. When boiled with sodium carbonate solution, the carbonate, or basic carbonates, form zinc oxide. Zinc, or zinc oxide, dissolves in water containing CO_2.

The **cyanide,** $Zn(CN)_2$, is formed as a white precipitate by precipitating zinc acetate with aqueous hydrocyanic acid. It is soluble in potassium cyanide, forming a complex salt, $K_2Zn(CN)_4 \rightleftharpoons 2K^{\cdot} + Zn(CN)_4''$.

Zinc nitrate, $Zn(NO_3)_2,6H_2O$, is a deliquescent salt, soluble in alcohol. **Zincamide,** $Zn(NH_2)_2$, is formed by the action of ammonia on zinc ethyl (*q.v.*): $Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6$. On heating to dull redness it forms the **nitride,** Zn_3N_2, a green powder vigorously decomposed by water: $Zn_3N_2 + 3H_2O = 3ZnO + 2NH_3$. The **phosphide,** Zn_3P_2, is a grey mass formed by direct combination of the elements on heating.

Zinc ethyl, $Zn(C_2H_5)_2$, is formed as a volatile, spontaneously inflammable liquid, by heating zinc with ethyl iodide and then distilling. Zinc ethyl iodide, $Zn(C_2H_5)I$, is first produced as a crystalline compound, which decomposes on heating: $2Zn(C_2H_5)I = Zn(C_2H_5)_2 + ZnI_2$.

Complex ammonia compounds are formed with zinc salts, similar to those of copper, *e.g.*, $Zn(NH_3)_4Cl_2,H_2O$, $Zn(NH_3)_4SO_4,H_2O$, $Zn(NH_3)_5SO_4$, etc. (*cf.* p. 818).

The **atomic weight,** 64·85 (H = 1), was found by the analysis of the pure bromide.

Estimation of zinc.—Zinc is **estimated** by precipitation as basic carbonate, ignition, and weighing as ZnO, or by electrolysis of an alkaline solution. In the volumetric method, it may be titrated with standard potassium ferrocyanide, uranium nitrate (p. 958) being used as outside indicator : $Zn_2Fe(CN)_6$ is precipitated, and excess of ferrocyanide then gives a brown colour with the uranium salt.

CADMIUM. Cd = 111·51.

Cadmium.—Most zinc ores contain small amounts of another metal, **cadmium,** which also occurs as sulphide in the rare mineral *greenockite*, CdS. Blende may contain 2–3 per cent. of cadmium, and calamine up to 3 per cent.

A certain specimen of zinc oxide, which had a yellow colour, although free from iron, was found by Stromeyer in 1817 to contain the oxide of a new metal, to which he gave the name **cadmium**, from *cadmia*, the old name for zinc. A similar specimen of zinc oxide used for pharmaceutical purposes had been confiscated because its solution gave a yellow precipitate, supposed to be arsenic sulphide, with H_2S. Hermann showed that this was cadmium sulphide.

Cadmium is more volatile than zinc ; the boiling-points of the metals in the zinc group decrease with rising atomic weight. The first portions of dust collecting in the receivers of zinc furnaces in which ores containing cadmium are reduced therefore contain most of the cadmium, in the form of brown oxide, CdO, mixed with zinc oxide. The dust is heated strongly with coal in retorts having long sheet iron cones as adapters. The distillate may contain 20 per cent. of cadmium, whilst the original oxides contain only 1–6 per cent. Finally, the product is distilled with charcoal in small iron or clay retorts.

Metallic cadmium is used as an amalgam as the cathode in the Weston standard cell. The amalgam is also applied in dental stoppings. Cadmium forms very fusible alloys with other metals ; *e.g.*, **Wood's fusible metal,** m.-pt. 61°, consists of 4 parts of bismuth, 2 each of tin and lead, and 1 of cadmium. Cadmium is a soft, bluish-white metal, sp. gr. 8·60, melting at 321°, and boiling at 778°. The vapour density corresponds with the formula Cd. The metal becomes brittle at 80° ; it is said to exist in two allotropic forms, with a transition point at 64·9°.

Cadmium compounds.—Cadmium dissolves slowly in dilute acids, with evolution of hydrogen and formation of cadmium salts, all of which, except the brown **oxide,** CdO, and the bright-yellow **sulphide,** CdS, are colourless. The **hydroxide,** $Cd(OH)_2$, is precipitated by caustic soda or potash from the solutions ; it is insoluble in excess, but dissolves in ammonia, forming a complex hydroxide, $Cd(NH_3)_4(OH)_2$. Cadmium is characterised by the readiness with which it forms **complex salts,** but this is even more marked in the case of mercury. Cadmium hydroxide attracts carbon dioxide from the air; the normal **carbonate,** $CdCO_3$, is precipitated from the salts by alkali carbonates (*cf.* Zn). On heating the hydroxide or carbonate, or by burning the metal in air, the brown **oxide,** CdO, is formed.

Of the soluble salts of cadmium, the **sulphate,** $3CdSO_4,8H_2O$, the solubility of which is nearly independent of temperature, and the **chloride,** $2CdCl_2,5H_2O$, which is efflorescent and is not hydrolysed by water (*cf.* $ZnCl_2$), are most important. The peculiar formulæ of the crystalline salts are noteworthy. The halogen salts are all soluble in water, but they are only very feebly ionised in solution, forming complex ions in which the metal exists in the negative ion: $2CdI_2 \rightleftharpoons Cd\cdot CdI_4 \rightleftharpoons Cd^{\cdot\cdot} + CdI_4''$. Insoluble cadmium salts, *e.g.*, CdS, therefore, readily dissolve in a solution of potassium iodide, since practically all the cadmium ions are removed as complex ions or un-ionised salts and the solubility product of the former salt is not exceeded: $Cd(OH)_2 + 2I' = CdI_2 + 2OH'$. If a concentrated solution of potassium iodide is added to an ammoniacal solution of a cadmium salt, a white precipitate of $Cd(NH_3)_2I_2$ is formed. Copper gives no precipitate. Complex cyanides are easily formed, *e.g.*, $K_2Cd(CN)_4$. **Cadmium iodide** is soluble in alcohol, and is used in photography.

Cadmium sulphide, CdS, is obtained as a bright yellow precipitate, used by artists under the name of *cadmium*, by passing sulphuretted hydrogen through a solution of a cadmium salt which is not too strongly acid. If the acid concentration exceeds 0·3 normal, the sulphide is not precipitated: $H_2S + CdSO_4 \rightleftharpoons CdS + H_2SO_4$.

Cadmium is separated from copper by boiling the precipitated sulphides with dilute sulphuric acid (1 : 5), when CdS dissolves; or by adding ammonia to the solution in excess, then potassium cyanide till colourless, and passing H_2S; CdS is precipitated.

Cadmium dissolves in a hot solution of cadmium chloride and on pouring into water a white precipitate of **cadmous hydroxide,** CdOH, is formed. (The solution probably contains CdCl.) On gently heating this, yellow **cadmous oxide,** Cd_2O, is obtained. Two other suboxides, Cd_4O and Cd_2O_2, are said to be formed on heating the oxalate.

Cadmium, the salts of which differ in many ways from those of magnesium and zinc, forms a bridge between these metals (which form only one series of compounds), and mercury, which forms two series of stable compounds, $\overset{I}{Hg}X$, or $\overset{II}{Hg_2}X_2$, and $\overset{II}{Hg}X_2$.

MERCURY. $Hg = 199{\cdot}0$.

Mercury.—Metallic **mercury,** which is peculiar in being liquid at the ordinary temperature, is first mentioned by Aristotle (B.C. 350); Theophrastus (B.C. 300) refers to it as *quicksilver*: *liquid silver* (*chutos argyros*); Dioscorides (1 A.D.) calls it *hydrargyros*. Pliny speaks of native mercury as *argentum vivum*, and the metal obtained by heating *cinnabar*, HgS, its important ore, with charcoal, as *hydrargyrum* (liquid silver). The metal was used in the extraction of gold.

The alchemists regarded mercury as the type of metallic properties; all metals, says Geber, are "composed of *Argentvive* and *Sulphur*, pure or impure" (p. 764). "By convenient *Preparation* 'tis possible to take away such Impurity . . . and supply the *Deficiency* in Perfect Bodies." Compounds of mercury, especially the violent poison *corrosive sublimate*, $HgCl_2$, first mentioned by Geber, were used by Paracelsus (1493–1541) and the Iatrochemists. Priestley employed a mercury trough in collecting gases which are soluble in water, and the metal was used by Lavoisier in his famous experiment on the analysis of air (p. 47). Mercury is used in the manufacture of barometers and thermometers, and its compounds corrosive sublimate, calomel (HgCl), and the fulminate, are used in the arts and in medicine. The truly metallic character of mercury does not seem to have been definitely admitted until the metal was frozen to a malleable solid (m.-pt. $-38{\cdot}8°$) by Braune in 1759. It is readily frozen by a mixture of solid carbon dioxide and ether.

Metallurgy of mercury.—Small quantities of mercury occur native, or as amalgams and halogen compounds, but the important ore is *cinnabar*, **mercuric sulphide,** HgS, a red mineral found in Carniola, Hungary, Peru, California, Mexico, Bavaria, China, and Japan. In the extraction of the metal the cinnabar is roasted in a current of air: $HgS + O_2 = Hg + SO_2$. The metal is not easily oxidised; it undergoes only slow oxidation in air at 300°.

In the older process of extraction, now used only at Almaden, the ore is roasted in a shaft, *B* (Fig. 408). The ore rests on a perforated arch, *k*, heated below by a fire, *A*. Air enters through *D*, and the vapours pass through six series of openings, *f*, into series of stoneware aludels (*cf.* p. 404), arranged first in a descending and then in an ascending position on brick arches. The condensed mercury flows from these into a channel, *b*, and then into cisterns. A little mercury vapour passing on is condensed in water, *i*, in the chamber, *C*. The metal is exported in iron bottles with screw stoppers. The modern furnaces differ according as lump or powdered ore is treated. Lump ore is roasted in admixture with charcoal in shaft furnaces, the mixture being fed continuously to the top of the shaft, as in limekilns, and the vapour of the metal condensed in **Y**-shaped earthenware pipes, cooled in water. Powdered ore is treated in Granzita furnaces, consisting of shafts containing inclined shelves, sloping at an angle of 45° in alternately opposite directions, over which the ore falls. Flames and air pass upwards in the opposite direction to the ore and heat the latter. The vapours pass to brick chambers, having cast-iron water-jackets for cooling, and then to glass and wooden towers. In these furnaces one ton of ore is worked in forty minutes. The annual production of mercury is about 3,500 tons, one-third coming from Spain.

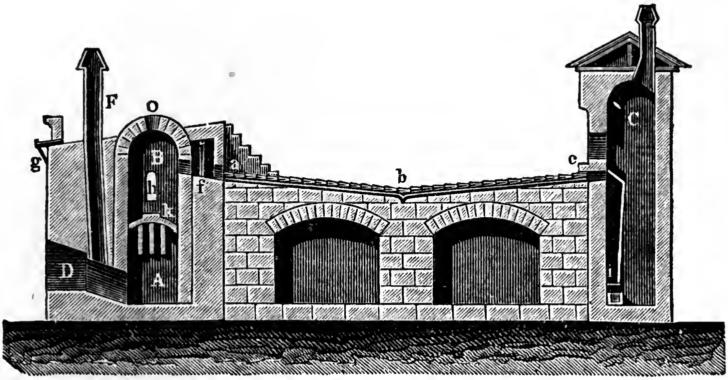


FIG. 408.—Extraction of Mercury at Almaden.

Properties of mercury.—Commercial mercury usually contains lead and copper. It then leaves a " tail " when allowed to run over an inclined glass surface, and forms a black scum of oxides when shaken with air in a stoppered bottle. The metal is **purified** by shaking with 5 per cent. nitric acid containing a little mercurous nitrate, or running it several times in a thin stream through this solution in the apparatus shown in Fig. 409. The metal is then distilled in a quartz flask under reduced pressure, a slow stream of air being allowed to bubble through the metal.

Mercury is a liquid metal with a silver-white colour. Its density at 0° is 13·5955, and at $-185°$, 14·383 ; it boils at 357·25°, and the vapour density corresponds with the formula Hg. The monatomicity of the vapour is proved by the ratio of specific heats, $c_p/c_v = 1{\cdot}667$, found by Kundt and Warburg from the measurement of the velocity of sound in the vapour at 360° (p. 599). Mercury is transparent in very thin films, and then transmits blue light. A **colloidal** form (*hygrol*) is obtained by the reduction of mercurous nitrate with stannous

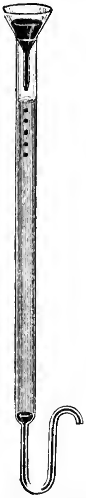


FIG. 409.—Purification of Mercury.

nitrate in presence of ammonium nitrate: the black precipitate dissolves in water to a brown solution.

When shaken with different liquids, or triturated with fats or powders such as sugar, the metal is converted into a grey powder, consisting of globules which may be as small as 0·002 mm. Grey mercury ointment is made in this way. The metal is not attacked by dilute hydrochloric or sulphuric acid, or alkalies, but dissolves in dilute nitric acid or hot concentrated sulphuric acid.

Mercury dissolves many metals, forming **amalgams,** which, when more than a certain amount of metal is present, are solid. Many of these contain definite compounds, *e.g.*, $NaHg_2$, KHg_2. Copper, silver, lead, gold, etc., are rapidly dissolved by mercury. Iron is not amalgamated under ordinary conditions, but an amalgam is formed by triturating iron powder with mercuric chloride and water. Mercury readily penetrates sheet copper, rendering it brittle. Copper amalgam becomes plastic when warmed to 100°, and rubbed in a mortar. After ten to twelve hours it again becomes hard. It is used for stopping teeth.

EXPT. 325.—Pour a little mercury into a solution of silver nitrate. A tree like growth of silver amalgam is produced (*arbor dianæ*).

Compounds of mercury.—Mercury forms two series of compounds, the **mercurous compounds,** HgX or Hg_2X_2, and the **mercuric compounds,** HgX_2. The former are obtained with an excess of metal. Thus, if excess of mercury is triturated with iodine, green **mercurous iodide,** HgI, is obtained; with excess of iodine, red **mercuric iodide,** HgI_2, is formed (p. 116). If mercury in excess is treated with cold dilute nitric acid, **mercurous nitrate,** $HgNO_3,H_2O$, crystallises out, whilst if mercury is boiled with fairly concentrated nitric acid, **mercuric nitrate,** $Hg(NO_3)_2$, is formed, which crystallises as $2Hg(NO_3)_2,H_2O$, on cooling.

The **constitution of the mercurous salts** has been the object of several experiments. H. B. Baker found that the vapour density of carefully dried mercurous chloride corresponded with the doubled formula Hg_2Cl_2, which was also found by Beckmann from the freezing-point of a solution of mercurous chloride in mercuric chloride. Ogg, from physico-chemical considerations, also concluded that the **mercurous ion** has the formula $Hg_2^{\cdot\cdot}$. The element, therefore, appears to be always bivalent, the mercuric compounds being HgX_2, whilst the mercurous compounds contain the group –Hg–Hg–, in which the metal also has a valency of two, and are therefore analogous to the cuprous compounds, containing –Cu–Cu– (p. 254). The vapour density of ordinary undried mercurous chloride corresponds with the formula HgCl, but Harris and Victor Meyer (1894) showed that the vapour was dissociated into a mixture of Hg and $HgCl_2$. If the vapour is contained in a porous earthenware tube, mercury diffuses out, and condenses in globules, whilst the residue in the tube contains an excess of $HgCl_2$. If a stick of potash is introduced into the vapour, a red coating of mercuric oxide, HgO, is formed on it, not black mercurous oxide, Hg_2O.

The tendency to form **complex compounds,** which is absent in the case of magnesium and zinc, but noticeable with cadmium, is very pronounced in the case of mercury. Numerous stable complex salts, containing oxygen, sulphur, and nitrogen, are known.

Mercurous compounds.—Mercurous nitrate, $HgNO_3,H_2O$, is formed by the action of dilute nitric acid on the metal in the cold, and readily crystallises from the solution on standing. If water is added to the crystals, a white precipitate of a basic nitrate is produced, which redissolves in dilute nitric acid. A little mercury is usually kept in the solution to prevent oxidation to the mercuric compound.

Chlorides or hydrochloric acid precipitate white **mercurous chloride,** HgCl, from the solution of mercurous nitrate. To obtain a pure product, excess of chloride is used, and the solution heated. This salt, called *calomel*, is of importance in medicine as a purgative. It is usually prepared by subliming a mixture of mercuric chloride and metallic mercury, made by triturating the substances in a mortar. This is heated in an iron pot, and the crust of calomel formed on the lid is ground to powder and boiled with water to remove the very poisonous mercuric chloride, some of which always sublimes unchanged.

Calomel is sparingly soluble in water (0·4 mgm. per litre at 20°; **mercurous fluoride,** HgF, is soluble in water). It dissolves to some extent in solutions of chlorides, or concentrated hydrochloric acid, but is decomposed, with deposition of mercury; complexes are formed in solution :

$$2HgCl + HCl \rightleftharpoons HHgCl_3 + Hg\,;\quad HHgCl_3 + HCl \rightleftharpoons H_2HgCl_4,$$

giving the ions $HgCl_3'$, and $HgCl_4''$.

Mercurous bromide, HgBr, is similar to calomel. The **iodide,** HgI, is formed as a green powder by triturating mercury and iodine (p. 116). On heating, it becomes yellow.

Mercurous sulphate, Hg_2SO_4, is formed by warming an excess of mercury with concentrated sulphuric acid (or oleum), and deposits as a coarsely crystalline powder on cooling. It is also formed as a white precipitate by adding sulphuric acid to a solution of mercurous nitrate. When excess of acid is removed by washing, hydrolysis of the salt commences, and with water at 25° a basic salt, Hg_2SO_4,Hg_2O,H_2O, is formed. Mercurous sulphate is used as a depolariser in the standard **Weston cell,** which gives a constant E.M.F. of 1·0186 volts, nearly independent of temperature, when made up with pure materials : $Cd + Hg_2SO_4 = CdSO_4 + 2Hg$.

Mercurous oxide, Hg_2O, is formed as a black powder by treating calomel with caustic soda solution. It decomposes at 100°, or on exposure to light, into yellow mercuric oxide and metallic mercury : $Hg_2O = HgO + Hg$.

Mercurous carbonate, Hg_2CO_3, is precipitated as a yellow powder on adding excess of potassium bicarbonate to mercurous nitrate solution, and allowing to stand for a few days to decompose any basic nitrate. It decomposes at 100° : $Hg_2CO_3 = HgO + Hg + CO_2$, or on exposure to light.

Mercuric compounds.—The mercuric compounds, HgX_2, are formed by the oxidation of mercurous compounds. Thus, calomel dissolves in *aqua regia*, forming **mercuric chloride,** $HgCl_2$. The mercuric compounds, conversely, may be reduced to mercurous compounds, or to metallic mercury. Thus, calomel is precipitated if sulphur dioxide is passed through a solution of mercuric chloride : $2HgCl_2 + 2H_2O + SO_2 = 2HgCl + 2HCl + H_2SO_4$. By the action of a solution of stannous chloride, white calomel, or grey finely-divided mercury, may be precipitated, according to the proportions added : $2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$; and with excess of $SnCl_2$: $2HgCl + SnCl_2 = 2Hg + SnCl_4$. All compounds of mercury are reduced to the metal if boiled with hydrochloric acid and copper foil ; the latter becomes white owing to amalgamation, and on heating the foil in a glass tube a sublimate of minute globules of mercury is formed. A similar sublimate is obtained directly if a mercury salt is heated with powdered charcoal and sodium carbonate.

Mercuric nitrate, $Hg(NO_3)_2$.—This salt is obtained in large, very deliquescent, colourless crystals, $2Hg(NO_3)_2,H_2O$, by boiling mercury with excess of concentrated nitric acid, cooling, and evaporating over concentrated sulphuric acid in a desiccator. The mother liquor on evaporation deposits a basic salt, $2Hg(OH)NO_3,H_2O$. Mercuric nitrate is decomposed by water ; at 25° the basic salt, $Hg(NO_3)_2,2HgO,H_2O$, is formed as a white powder, decomposed into oxide by further action of water. Mercuric nitrate is precipitated by concentrated nitric acid from its aqueous solution.

Mercuric sulphate $HgSO_4$, is obtained by boiling mercury with one and a half times its weight of concentrated sulphuric acid, and evaporating to dryness. The white residue may be crystallised from sulphuric acid. With a *small* quantity of water, the residue forms colourless crystals of $HgSO_4,H_2O$, but it readily hydrolyses, producing at 25° a basic salt, which is a yellow, crystalline powder, $3HgO,SO_3,4H_2O$, sparingly soluble in water, and called *turpeth mineral.* This was described by Basil Valentine.

Mercuric oxide, HgO.—By adding an alkali to a solution of the nitrate, **mercuric oxide,** HgO, is precipitated ; from cold solutions this separates as a yellow, from hot solutions as an orange, powder. According to Ostwald, the difference in colour is due merely to differences in the fineness of the powder, but Schoch states that the two varieties have different crystalline forms, and different dissociation pressure at 300°. By heating the nitrate, alone or intimately mixed with mercury, to a moderate temperature, the crystalline red oxide is formed. A dense red crystalline oxide is also formed slowly on heating mercury in an open flask with a long neck at about 300°. This form, described by the Latin Geber, was called by the alchemists *mercurius præcipitatus per se*, or "red precipitate." It decomposes on heating (p. 24); if the mercury is kept from condensing, an equilibrium is set up: $2HgO \rightleftarrows 2Hg + O_2$.

Mercury peroxide, HgO_2, is obtained as an amorphous, brick-red powder when hydrogen peroxide and then alcoholic potash are added to a solution of mercuric chloride in alcohol. It is fairly stable, but is decomposed by water. The peroxide is also formed by the action of H_2O_2 on HgO, but decomposes with evolution of oxygen, leaving finely-divided mercury.

Mercuric chloride, $HgCl_2$.—Mercury is rapidly attacked by chlorine, a white crust of **mercuric chloride,** $HgCl_2$, forming on the metal. The action is more rapid if the mercury is heated. Mercuric chloride is also called *corrosive sublimate* on account of its very poisonous properties, and its volatility (m.-pt. 286°; b.-pt. 303°; sp. gr. 5·41). The fatal dose is 0·2–0·4 gm.; the antidote is the immediate administration of raw whites of eggs, followed by an emetic. The albumin is coagulated. Corrosive sublimate is used in preserving skins, as a bactericide, and medicinally: a 0·1 per cent. solution is used for sterilising the hands and instruments in surgery.

The preparation of corrosive sublimate is described by the Latin Geber, who obtained it by subliming a mixture of finely-divided mercury, calcined green vitriol, common salt, and nitre:

$$Hg + 2NaCl + 2KNO_3 + Fe_2S_2O_9 = HgCl_2 + Na_2SO_4 + K_2SO_4 + Fe_2O_3 + 2NO_2.$$

The use of mercury compounds in medicine was introduced by Paracelsus, and by the end of the sixteenth century corrosive sublimate was sold by most druggists. Lemery describes its preparation by the sublimation of mercuric nitrate (obtained by evaporating a solution of mercury in nitric acid) with common salt and calcined green vitriol, but the modern process of manufacture was first suggested by Kunckel in 1670. Mercuric sulphate, obtained by evaporating to dryness a solution of mercury in hot concentrated sulphuric acid, is mixed with an equal weight of common salt. The mixture, to which a little manganese dioxide is added, is sublimed on a sand-bath in long-necked, flat-bottomed flasks : $HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4$. The flasks are cooled, broken, and the cakes of sublimate removed from the upper parts. Mercuric chloride forms colourless, rhombic needles, sparingly soluble in cold, but readily in hot water : 100 parts of water dissolve at 0° 4·3, at 10° 6·57, and at 100° 54 parts of $HgCl_2$. The salt is only slightly ionised in solution ; less than 1 per cent. is dissociated in decinormal solution, whilst more than 90 per cent. is the usual ionisation of salts at this dilution. Mercuric chloride is readily soluble in alcohol and in ether ; if an aqueous solution is shaken with ether, most of the salt passes into the ethereal layer.

On account of the small ionisation of the salt, mercuric chloride is not decomposed by boiling concentrated sulphuric acid, but sublimes unchanged. It is also unacted upon by nitric acid. The solution of mercuric chloride contains the complex ions $HgCl^{\cdot}$, $HgCl_3'$, and $HgCl_4''$. The salt dissolves with evolution of heat in concentrated hydrochloric acid ; the resulting solution does not fume, and on cooling deposits crystals of **hydrochloromercuric acid,** $HHgCl_3$. With chlorides of alkali-metals a number of crystalline compounds are formed, *e.g.*, $KHgCl_3$ and Na_2HgCl_4, which are partly decomposed in solution, and partly ionised into complex ions : $Na_2HgCl_4 \rightleftarrows 2Na^{\cdot} + HgCl_4''$. A solution of Na_2HgCl_4 is used instead of $HgCl_2$ as an antiseptic, since it is neutral in reaction and does not coagulate proteins.

Alkalies precipitate a solution of mercuric chloride only incompletely, and mercuric oxide readily dissolves in solutions of alkali-chlorides, forming strongly alkaline liquids : $HgCl_2 + 2NaOH \rightleftarrows HgO + 2NaCl + H_2O$. This depends on the small ionisation of mercuric chloride, the concentration of mercuric ions from the dissociation of which is less than that in the very dilute saturated solution of mercuric oxide. The latter, therefore, dissolves with formation of un-ionised chloride.

Mercuric chloride is readily reduced by various reagents, a white precipitate of calomel or a grey precipitate of metallic mercury being formed. Stannous chloride produces HgCl or Hg, according to the amount added. A mixture of mercuric chloride solution and oxalic acid is reduced (in presence of minute traces of iron salts) on exposure to light with measurable velocity depending on the intensity of the light : $2HgCl_2 + C_2O_4H_2 = 2HgCl + 2CO_2 + 2HCl$. Since the calomel may be filtered off and weighed, the reaction is used as a **chemical photometer** (Eder).

Phosphorus pentachloride combines with mercuric chloride to form the volatile crystalline compound, $3HgCl_2,2PCl_5$.

By boiling a solution of mercuric chloride with mercuric oxide, a series of **oxychlorides** is formed, *e.g.*, $2HgCl_2,HgO$, red ; $HgCl_2,2HgO$, black ; $HgCl_2,3HgO$ (*kleinite*), yellow.

Mercuric fluoride, HgF_2, unlike the other halogen compounds, is hydrolysed and forms a basic salt, $HgF(OH)$, with water.

Mercuric bromide, $HgBr_2$, is similar to the chloride.

Mercuric iodide, HgI_2.—This salt is formed as a yellow precipitate, which rapidly becomes scarlet, on adding the calculated amount of potassium iodide to mercuric chloride solution. On heating to 126°, it is converted into another crystalline form, which is yellow. The reverse change occurs on cooling, especially if the substance is rubbed. The yellow form is deposited on sublimation. The iodide is difficultly soluble in water (1 in 25,000), but readily in alcohol. It is not decomposed by dilute alkalies.

Mercury periodide, HgI_6, is a brown substance obtained by the action of mercuric chloride on an alcoholic solution of potassium tri-iodide. It readily loses iodine.

Mercuric iodide readily dissolves in solutions of mercuric chloride or potassium iodide. In the second case, a complex compound, potassium mercuri-iodide, K_2HgI_4, is formed, and can be obtained as a pale yellow solid on evaporation. The solution is not precipitated by bases, since practically no mercuric ions are present, and mercuric oxide dissolves in a solution of potassium iodide to form a strongly alkaline liquid : $HgO + 4KI + H_2O = K_2HgI_4 + 2KOH$.

A solution of potassium mercuri-iodide containing excess of caustic potash is used as a test for ammonia under the name of **Nessler's reagent.**

This is prepared by dissolving 62·5 gm. of potassium iodide in 250 c.c. of distilled water, and adding to the solution, except 5 c.c. which is separated, a cold saturated solution of mercuric chloride until a faint permanent precipitate is formed. About 500 c.c. will be required. The 5 c.c. of KI solution are then added, and more $HgCl_2$ gradually until a slight permanent precipitate is again formed. 150 gm. of caustic potash are dissolved in 150 c.c. of distilled water and the cooled solution added gradually to the other solution. The whole is made up to 1 litre. After settling, the clear solution, which should have a slight yellow colour, is decanted into a bottle covered with black varnish. It improves on keeping. With traces of ammonia a brown colour, with larger amounts a brown precipitate, of NHg_2I is formed.

By adding a solution of HgI_2 in liquid ammonia to an excess of potassamide, KNH_2, dissolved in liquid ammonia, a chocolate-brown precipitate of **mercuric nitride,** Hg_3N_2, is formed. The **acetylide,** $3C_2Hg,H_2O$, is formed as a white precipitate on passing acetylene into a solution of mercuric oxide in aqueous ammonia. The **cyanide,** $Hg(CN)_2$, which is only slightly ionised, is formed by dissolving HgO in aqueous HCN, and crystallising ; it is used in the preparation of cyanogen: $Hg(CN)_2 = Hg + C_2N_2$. The **thiocyanate,** $Hg(CNS)_2$, is formed as a white precipitate on adding KCNS to $HgCl_2$ solution; when made into small pills and lit with a taper it gives a long, snake-like mass of *mellon,* a polymerised cyanogen product (*Pharaoh's serpent*).

Mercuric carbonate is known only in the form of **basic** salts; from a solution of mercuric nitrate, K_2CO_3 gives a brown precipitate of $HgCO_3,2HgO$; $KHCO_3$ gives a brown precipitate of $HgCO_3,3HgO$.

Mercuric sulphide, HgS.—The sulphide, HgS, which occurs as *cinnabar,* is the pigment *vermilion.* It is formed by triturating mercury and sulphur with a little caustic potash solution. The black, amorphous sulphide produced becomes red and crystalline on sublimation. Mercuric sulphide is formed by precipitating a solution of the chloride with sulphuretted hydrogen: $HgCl_2 + H_2S = HgS + 2HCl$. The black precipitate of HgS first formed becomes white if shaken with the excess of mercuric chloride solution, the compound $Hg(HgS)_2Cl_2$ being produced. The further action of H_2S changes this into a red and finally a black (HgS) precipitate. The black precipitate becomes red on sublimation. It is insoluble in boiling hydrochloric or dilute nitric acid, but dissolves in *aqua regia* or in solutions of alkali-sulphides. In the second case thio-salts, *e.g.,* $K_2HgS_2,5H_2O$ (white needles), are formed. The red form of the sulphide is less soluble in alkali sulphides than the black variety; the latter when digested with sodium sulphide solution is slowly converted into scarlet vermilion. Mercuric sulphide burns when heated in air: $HgS + O_2 = Hg + SO_2$. It is decomposed by heated iron filings: $HgS + Fe = FeS + Hg$ (*cf.* manufacture of mercury).

Mercuric fulminate, $Hg(ONC)_2$, is obtained as a white precipitate on warming a solution of mercury in excess of nitric acid with alcohol. It is used in making detonators, since it explodes on percussion. It is now being replaced to some extent by lead azide, $Pb(N_3)_2$.

Mercurammonium compounds.—By the action of ammonia gas on mercuric chloride, a compound $HgCl_2,2NH_3$, called *fusible white precipitate,* is obtained. This is also formed as a white precipitate by adding a solution of mercuric chloride to a boiling solution of ammonium chloride and ammonia. It was formerly regarded as mercur-diammonium chloride, $Hg(NH_3Cl)_2$, but is probably an additive compound. If ammonia is added to a solution of mercuric chloride, mercuric oxide is not obtained, as with potash or soda, but a white precipitate of **mercurammonium chloride,** NHg_2Cl, *i.e.,* ammonium chloride, NH_4Cl, in which four atoms of hydrogen are replaced by two atoms of bivalent mercury, is formed. This is called *infusible white precipitate.* The brown precipitate obtained by the action of ammonia on Nessler solution is **mercurammonium iodide,** NHg_2I.

If mercuric oxide is gently warmed with aqueous ammonia, a yellow powder known as **Millon's base** is formed. According to Rammelsberg (1888), this is the hydroxide corresponding with the mercurammonium salts, $NHg_2{\cdot}OH,2H_2O$. On drying at 125° in ammonia gas, dark-brown explosive $NHg_2{\cdot}OH$ is formed. Hofmann and Marburg (1899) formulate Millon's base as $(HOHg)_2NH_2{\cdot}OH$. Compounds isomeric with the salts of Millon's base were prepared by Franklin (1907) by the action of liquid ammonia on $HgBr_2$ and HgI_2; he regards them as amino-compounds, $Hg{:}N{\cdot}HgX$.

By the action of aqueous ammonia on calomel, a black powder is formed, which is a mixture of infusible white precipitate and finely-divided mercury, $Hg + HgNH_2Cl$. A similar black precipitate is formed by adding ammonia to a solution of mercurous nitrate, $Hg + HgNH_2{\cdot}NO_3$. The formation of this black powder from calomel is said to be the origin of the name of the latter, from the Greek *kalomelas*, beautiful black. Dry calomel absorbs ammonia gas, forming the additive compound $HgCl,NH_3$.

If mercuric oxide is dissolved in a solution of potassium nitrite, and the solution is neutralised with acetic acid, a beautifully crystallised bright yellow salt, soluble in water, is formed. This is **potassium mercurinitrite,** $K_2Hg(NO_2)_4$, and is very stable.

Phosphorescence.—Reference has been made to the **phosphorescence** of calcium sulphide and nitrate, barium and zinc sulphides, *i.e.*, the property of which these materials possess of shining after exposure to light, especially sunlight. This is utilised in the preparation of *luminous paint*. Apart from a single unconfirmed observation, it has always been found that pure compounds do not exhibit phosphorescence; the latter is due to traces of heavy metals such as bismuth, lead, copper, molybdenum, tungsten, uranium, etc. Thus, phosphorescent calcium sulphide is obtained by heating a mixture of 100 parts of calcium carbonate with 30 parts of powdered sulphur for an hour to dull redness in a closed crucible. The mass is cooled, and triturated with alcohol to which sufficient bismuth nitrate is added to give 1 part of bismuth to 10,000 of calcium sulphide. The mass is dried in the air, and heated to dull redness for two hours. It is then slowly cooled.

Other phosphorescent masses are prepared by heating the mixtures *A* below, powdering the product, moistening with the solutions *B*, and reheating:

1. *Violet light*: *A*: CaO (powder) 20, S 6, starch 2, Na_2SO_4 0·5, K_2SO_4 0·5. *B*: 2 c.c. of 0·5 per cent. $Bi(NO_3)_3$ solution + 0·5 c.c. of aqueous Tl_2SO_4.
2. *Deep blue light*: *A*: CaO 20, $Ba(OH)_2$ 20, S 6, K_2SO_4 1, Na_2SO_4 1, Li_2CO_3 2, starch 2. *B*: 2 c.c. of 0·5 per cent. alcoholic $Bi(NO_3)_3$ solution + 2 c.c. of 1 per cent. $RbNO_3$ solution.

3. *Bright green light* : *A* : $SrCO_3$ 40, S 6, Li_2CO_3 1, As_2S_3 1. *B* : 2 c.c. of 0·5 per cent. $TlNO_3$ solution.

4. *Deep orange-red light* : *A* (only) : $BaCO_3$ 40, S 6, Li_2CO_3 1, Rb_2CO_3 0·47.

Lenard explains phosphorescence by supposing that under the action of light, electrons are emitted from the sulphides of the heavy metals, *e.g.*, bismuth, but these electrons are retained by the mass of calcium or barium sulphide. In the dark the electrons return to the molecules from which they came, and light is emitted when the electron enters the molecule.

EXERCISES ON CHAPTER XLI

1. Describe the general properties of the sub-group, Be, Mg, Zn, Cd, Hg. What analogies do beryllium and mercury show to elements of other groups ?

2. How may a beryllium salt be obtained from beryl ? How has the atomic weight of beryllium been decided ?

3. In what forms does magnesium occur ? How are Epsom salts and magnesium chloride made, and for what purposes are they used ?

4. Describe the preparation of : (*a*) magnesium, (*b*) anhydrous magnesium chloride, (*c*) magnesium nitride. What is the action of water on these substances ?

5. What are calcined magnesia, magnesia alba, and dolomite ? For what purposes are they used ?

6. Describe the methods used for the extraction of zinc from its ores, and for the purification of the metal.

7. How is zinc oxide prepared ? What is the action of (*a*) dilute sulphuric acid, (*b*) ammonia, (*c*) ammonium sulphide, upon it ?

8. What are lithopone, Rinman's green, turpeth mineral, calomel, blende, cinnabar, greenockite, fusible white precipitate, *mercurius præcipitatus per se* ?

9. How are the following prepared : zinc carbonate, mercurous nitrate, mercuric iodide, cadmium sulphide ?

10. How is mercury obtained from its ores, and how is the metal purified ?

11. How are corrosive sublimate and calomel prepared from mercury ? What is known as to the vapour density of calomel and the constitution of mercurous salts ?

12. What is the action of ammonia on (*a*) mercuric chloride, (*b*) mercuric oxide, (*c*) calomel ? What is Nessler's reagent, and what is its action on ammonia ?

CHAPTER XLII

VOLTAIC CELLS

Electrical energy.—The decomposition of electrolytes by an electric current is accompanied by an absorption of energy, derived from the battery or other arrangement used in supplying the current. In batteries, chemical reactions take place, as a result of which chemical energy is transformed into **electrical energy**: this process may be considered as the inverse of electrolysis. Some chemists have gone so far as to suppose that *all* chemical changes are really cases of reversed electrolysis, but it is evident that the only changes which can furnish electric currents when carried out in suitable ways are those involving electrically charged **ions,** and there is no reason to suppose that all reactions must occur between ions.

In a chemical reaction as usually carried out there is generally a liberation of energy in the form of **heat,** derived from the change of **chemical energy** resulting from the atoms falling into new modes of combination. At first sight it might be supposed that if the reaction could be carried out so as to produce electrical energy instead of heat, the former should be equivalent to the latter. This is not generally the case. The heat evolved in a reaction which takes place at constant volume is a measure of the change of **total energy** in the reacting substances (p. 387). If the reaction is allowed to take place so as to produce an electric current it is found that the energy value of the latter may be less than the change of total energy, in which case the balance is given out as heat, or in some cases it may be greater than the change of total energy, in which case the cell absorbs heat from the outside to make up the balance. The energy of the current is called the **free energy** of the reaction, since it may be wholly converted into useful work by means of an electric motor. The free and total energies of a reaction are not usually equal.

It was formerly assumed that the heat of reaction, *i.e.*, the diminution of total energy, was a measure of the work done by the chemical affinities of the interacting substances, *i.e.*, a measure of **affinity.** It is now known that the free energy change is the correct measure of the affinity. The measurement of changes of free energy is most conveniently effected by the electrical method, and the latter is therefore of great importance in chemistry. The question : " What is the affinity of a reaction ? " is equivalent to the question : " What is the maximum electrical energy which the given reaction can yield ? "

Voltage.—Although Faraday's second law shows that the same **quantity of electricity,** viz., 96,000 coulombs, is required in the decomposition of one gram-equivalent of a compound into its uncharged ions (p. 279), the amounts of **electrical work** which must be spent in the decomposition of various compounds are very different, corresponding with the different affinities. The reason is that the electrical energy depends on something besides the quantity of electricity. The decomposition of a gram-molecule each of hydrochloric acid and hydriodic acid requires electrical energy equivalent to 39,300 cal. and 13,100 cal. respectively. Just as the energy of a stream of water is represented by the product of the volume flowing past a given section per second and the pressure or head of water available, so the energy of an electric current is given by the product of the quantity of electricity transported by the current and the **electrical pressure,** which drives the electrons composing the current. This electrical pressure is called **electromotive force,** or **voltage.** The pressure of water may exist whether the stream is flowing or not, and the electric pressure may also exist between the poles of a battery when the latter is not giving any current, and may be detected by a sensitive electroscope ; it sets the current in motion as soon as the poles of the battery are joined by a wire through which the electrons may be driven. The electric pressure is measured in **volts** ; this unit is defined in such a way that the quantity of electricity transported in coulombs, multiplied by the pressure in volts, gives the electrical energy in **joules,** where 1 joule = 10^7 ergs :

$$\textbf{Volts} \times \textbf{Coulombs} = \textbf{Joules.}$$

The work done per second is equal to the quantity of electricity moved per second multiplied by the voltage. But the quantity of electricity moved per second is the current strength in amperes (p. 282), so that the rate at which work is done by the current, or the **power,** is measured by the product of the amperes and volts. The unit of power, 1 joule per second, is called a **volt-ampere,**, or a **watt :**

$$\textbf{Volts} \times \textbf{Amperes} = \textbf{Watts.}$$

The watt is a small unit, so that in practice the **kilowatt,** or 1,000 watts, is used. Energy is then measured in **kilowatt hours** (K.W.H.), or the number of kilowatts expended per hour. It is easily seen that 1 K.W.H. = volts × amperes × 3600/1000.

An ordinary metal-filament lamp uses 220 volts at about half an ampere. The power consumed is $220 \times \frac{1}{2}/1000 = 0{\cdot}11$ K.W., or 110 watts. If the lamp is 220 candle-power, it uses $\frac{1}{2}$ watt per candle, and is called a "half-watt lamp." Again, 1 cal. $= 4{\cdot}186 \times 10^7$ erg $=$ 4·186 joules. Thus 1 volt-amp.-sec. $=$ 1 joule $=$ 0·238 cal. The voltages required to decompose hydrochloric and hydrobromic acids are, on the basis of the numbers given above:

$$\text{HCl}: \quad 39{,}300 \times 4{\cdot}186 \div 96{,}000 = 1{\cdot}73 \text{ volts};$$
$$\text{HBr} \quad 13{,}100 \times 4{\cdot}186 \div 96{,}000 = 0{\cdot}57 \text{ volt};$$

since in each case the quantity of electricity involved is 96,000 cmb.

Voltaic cells.—An arrangement in which chemical energy is converted into electrical energy is called a **voltaic cell,** since the first representative of this type of apparatus was invented by Volta in 1800. There are many types of such cells, the description of which belongs to the study of electricity, but one or two representative forms will be considered so as to make clear the conditions under which the conversion of chemical into electrical energy takes place.

The earliest type of cell, devised by Volta, consists of a plate of zinc and one of copper immersed in dilute sulphuric acid. When the plates outside the liquid are joined by a wire, the zinc dissolves, but the hydrogen bubbles are evolved from the copper, not from the zinc. An **electric current,** recognised by its heating and magnetic effects, flows through the wire. The direction of flow of positive electricity is taken conventionally as the direction of the current, although it is really negative electricity, in the form of **electrons,** which flows through conductors (p. 281). With the usual convention the direction of the current is from the copper to the zinc outside the cell. Since the current must be completed inside the cell, the positive electricity passes in the latter from the zinc to the copper. This is effected by the transport of positive charges by the hydrogen ions moving in this direction. The hydrogen ions are deposited on the copper plate, give up their charges to it, and appear as gaseous hydrogen. The discharge may be regarded as due to the removal of free electrons from the copper plate, which neutralise the positive hydrogen ions: $\text{H}^{\cdot} + \epsilon = \text{H}$.

The negative charge taken from the copper is replaced by a current of negative electrons flowing along the wire from the zinc to the copper, *i.e.*, in the opposite direction to the conventional positive current. These electrons must come from the zinc. The latter dissolves as positively charged zinc ions, and the positive charges of the latter are derived by the abstraction of electrons from the zinc atoms: $\text{Zn} - 2\epsilon = \text{Zn}^{\cdot\cdot}$. These electrons remaining in the zinc pass along the wire to, and neutralise the hydrogen ions arriving at, the copper plate.

If the zinc had merely dissolved in the acid without producing current, the hydrogen ions of the acid would have been neutralised in contact with the metal when the latter passed into solution in the ionic state, and hydrogen gas would have been evolved from the surface of the zinc. In the cell, the neutralisation of the hydrogen ions, with production of hydrogen gas, still takes place on account of the negative charge left by the ionisation of the zinc, but the hydrogen ions have to travel through the liquid to the copper plate in order to pick up this charge, so that the two reactions, which when they take place in the same place give out only heat, when they are compelled to take place at two different localities produce a current.

Ordinary zinc contains traces of other metals, such as iron, and the specks of these metals lying on the surface of the zinc act like copper plates in the cells. Hydrogen gas is really given off from the second metal, and the current (which passes round the wire in the cell) flows through the zinc from the points where solution occurs to the parts where the impurities lie on the surface. Action of this kind is called **local action.** If the surface of the zinc is amalgamated, or if very pure zinc is used, the impurities are removed, and the surface is uniform. The metal then no longer evolves hydrogen in dilute acid, since local action is no longer possible. If, however, the zinc is touched under the surface of the acid with a piece of copper, or a platinum wire, bubbles of hydrogen are at once evolved from the wire, and the zinc dissolves. The copper–zinc couple (p. 182) is really a collection of little cells, in which local action takes place. The addition of a little copper sulphate to the zinc and dilute acid in the preparation of hydrogen (p. 184) is another instance of local action (*cf.* tinplate, p. 913, and galvanised iron, p. 862).

The voltaic cell does not generate *electricity*. The electrical charges are present in the chemical substances used in making up the cell, in the form of electrons, and the electrons are added to, or subtracted from, atoms to form ions. Some of these ions (*e.g.*, hydrogen ions) are discharged in the cell, and other previously uncharged substances (*e.g.*, zinc) are converted into ions. The electrons leaving one atom and attaching themselves to another are driven round the outside conducting wire. All the electrons remain in the materials of the cell, but in new combinations, and none are set free. During this transfer of electricity, *energy* may be taken from the battery. The connecting wire becomes heated, it acts upon magnets in its vicinity, and if it is cut and the ends are immersed in an electrolyte, the latter is decomposed. These processes involve the expenditure of energy.

The voltage of the Volta cell is about 0·74; a large number of these cells connected in series, *i.e.*, with the zinc of one connected with the copper of the next, formed the battery used by Davy in 1807 for the decomposition of the alkalies (p. 774).

The Daniell cell.—The Volta cell has the disadvantage that its voltage rapidly decreases when current is taken from it. In another type of cell, invented by Daniell (1836), the voltage remains practically constant during action. This cell consists (Fig. 410) of a rod of amalgamated zinc immersed in dilute sulphuric acid, and a plate of copper immersed in a solution of copper sulphate. The two solutions are separated by a pot of unglazed earthenware, which prevents them from mixing but permits the passage of ions moving from one liquid to the other. The voltage of this cell is about 1·09.

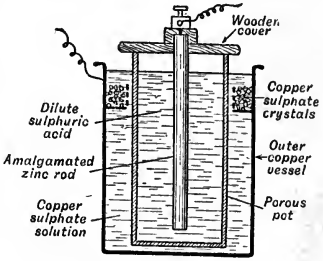


FIG. 410.—Daniell Cell.

The action of the Daniell cell is as follows. The zinc dissolves in the dilute acid as zinc ions, and the copper ions deposit from the copper sulphate solution as metal. No gas is evolved, since the hydrogen ions passing from the liquid round the zinc, through the porous partition, are not deposited but remain in the copper sulphate solution. Instead of hydrogen ions being deposited on the copper, copper ions, which are more easily discharged, give up their charges to, and form a coating of copper on, the copper plate. For every equivalent of copper deposited, an equivalent of hydrogen ions enters the copper sulphate solution, forming sulphuric acid, leaving an equivalent of SO_4'' ions in the zinc compartment, which form zinc sulphate with the zinc ions given off by the zinc plate. The dilute sulphuric acid is therefore gradually converted into a solution of zinc sulphate, whilst the copper sulphate solution is converted into dilute sulphuric acid.

The net reaction in the cell is the transfer of two unit positive charges from the copper ions to metallic zinc, whereby metallic copper and zinc ions are formed : $Cu^{\cdot\cdot} + Zn = Cu + Zn^{\cdot\cdot}$. Since both ions are bivalent, the reaction involves the transfer of $2 \times 96{,}000$ coulombs, and since the voltage of the cell is 1·1, the free energy of the reaction is $1{\cdot}1 \times 2 \times 96{,}000 = 211{,}200$ joules, which is equivalent to $211{,}200/4{\cdot}18 = 50{,}525$ gm. cal. The heat evolved in the displacement of copper from a solution of copper sulphate by one gm. atom of zinc : $Zn + CuSO_4 = ZnSO_4 + Cu$, or : $Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu$, is found experimentally to be 50,100 gm. cal. In this case, therefore, the **free energy** change is about the same as, but slightly greater than, the **total energy** change. This agreement is exceptional ; in most cells the two quantities are different ; they may even differ in sign.

Zinc in a solution of zinc sulphate, and copper in a solution of copper sulphate, separated by a porous partition, will also give a current, and may be considered as a modification of the Daniell cell. In this case the ion SO_4'' migrates from the $CuSO_4$ to the $ZnSO_4$ solution. Copper is deposited from the first solution, and zinc dissolves in the second. The former becomes less, and the latter more, concentrated in the operation of the cell.

If an external voltage slightly greater than 1·1 volts is applied to the terminals of a Daniell cell in the opposite direction to the voltage of the cell, the chemical reactions in the latter are reversed. Zinc is deposited and copper dissolves. This reaction must involve the absorption of energy by the cell, and since the reversing voltage need only be infinitesimally greater than the voltage of the cell, the energy spent in reversing the changes in the cell is, in the limit, equal to that given out in the direct operation of the cell. A cell of this type is called a **reversible cell.** Determinations of chemical affinity obviously presuppose that the cells are operating reversibly.

Electrode potentials.—If in the Daniell cell the zinc is replaced by another metal, such as cadmium, the other half of the cell remaining the same, the voltage changes. This is because the change of free energy in the new reaction : $Cd + Cu^{\cdot\cdot} = Cd^{\cdot\cdot} + Cu$, is different from that in the former reaction : $Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu$. If the zinc half of the cell is retained but silver in silver sulphate solution is substituted for copper in copper sulphate, there is, for the same reason, a change in voltage. **The voltage of a cell**, therefore, **depends on the nature of both its electrodes**, *i.e.*, of the metals and solutions.

The voltage also depends on the concentration of the ions in the solutions around the two electrodes. If the zinc sulphate solution around the zinc is diluted, or the copper sulphate solution around the copper made more concentrated, the voltage in each case increases. If a series of Daniell cells composed of Zn in a solution of $ZnSO_4$ containing 1 gm. equiv. of $Zn^{\cdot\cdot}$ ions per litre, and other metals in solutions also containing the unit concentration of metal ions, are made up, different voltages will result. If a cell composed of two of these other metals in their solutions, say Cu and Cd, is made up, its voltage will be found to be the difference between the voltages of two Daniell cells, composed of Zn and the metals Cu and Cd, respectively. The voltage of a cell may thus be regarded as the algebraic difference of two single voltages, one corresponding with each electrode. These are called **electrode potentials.**

Electrolytic solution pressure.—The source of the electrode potentials may be explained by Nernst's theory of **electrolytic solution pressure.** A bar of zinc immersed in water, dilute acid, or a solution of zinc sulphate tends to throw off zinc ions into the solution. This tendency is called the **solution pressure of the metal.** But the zinc ions in the solution exert an osmotic pressure, and tend to redeposit on the metal. As a result of the first change,

$Zn \rightarrow Zn^{\cdot\cdot}$, the metal will acquire a negative charge, and the solution containing the zinc ions thrown off, a positive charge. This reaction is soon brought to a standstill by the attraction of the opposite charges, so that a layer of positive zinc ions, which retain their charges, is attracted to the surface of the negative zinc plate (Fig. 411).

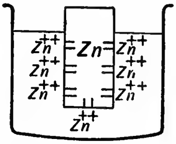


FIG. 411.—Diagram illustrating Formation of Electrical Double Layer.

The more zinc ions there are in the solution, the greater is their tendency to deposit on the metal, reducing its negative charge, so that the solution pressure of the metal is opposed and finally balanced by the **osmotic pressure of the ions** in solution. The greater the osmotic pressure, the fewer zinc atoms pass out into the solution as ions, and the smaller is the electrode potential developed. Beyond a certain concentration of ions, these tend to discharge on the zinc, and the latter is charged positively.

If a bar of copper is placed in a solution of copper sulphate, the copper ions of the latter tend, by their high osmotic pressure, which is opposed by a relatively small solution pressure, to deposit on the metal, giving up their charges. The metal becomes charged positively, leaving the solution negatively charged from withdrawal of positive ions, but the formation of a layer of negative ions on the surface of the metal again puts a stop to this reaction after a certain point.

If the two single electrodes, zinc and copper, are put in communication by a porous partition between the solutions, as in Fig. 412, we have a Daniell cell. The voltage of this is the algebraic difference of the single potential differences. The positively charged copper, the solution pressure of which is small, tends to drive a positive current round from the copper to the zinc outside the cell, if the metals are connected by a wire. The negatively charged zinc, the solution pressure of which is great, tends to drive a negative current in the opposite direction to, *i.e.*, a positive current in the same direction as, the copper. The ultimate source of the current may be regarded as the superior tendency of the zinc to force out its ions into the solution.

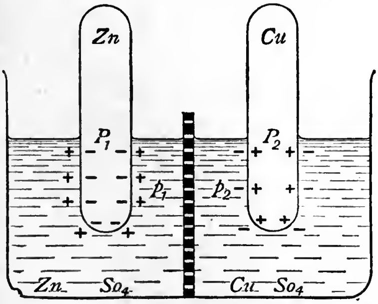


FIG. 412.—Theory of Action of Galvanic Cell.

The **single potentials** of metals in solutions of their ions containing 1 gm. equiv. per litre are given in the table below. The sign attached to the number of volts is that of the charge of the *solution*. Thus, zinc tends, in a normal solution of its ions, to throw out still more ions until the solution has a positive potential 0·5 volt higher than that of the metal. Copper ions, on the other hand, will tend to deposit from a normal solution, leaving the latter negatively charged at 0·6 volt below the metal. This table is called the **electromotive series.** Hydrogen is included, since when dissolved in platinum or palladium it acts like a metal electrode to solutions of acids, containing $H^{\cdot}$ ions.

Electromotive series of the metals.

K	(+2·6)	Fe($Fe^{\cdot\cdot\cdot}$)	+0·2	Bi	−0·63?
Na	(+2·4)	Cd	+0·16	Sb	−0·71
Ba	(+2·6)	Co	+0·05	Hg($Hg^{\cdot}$)	−0·99
Sr	(+2·5)	Ni	−0·02?	Pd	−1·03?
Ca	(+2·4)	Pb	−0·12	Ag	−1·04
Mg	+1·3	Sn($Sn^{\cdot\cdot}$)	−0·14	Pt	−1·10?
Al	+1·03	H	−0·24	Au	−1·7?
Mn	+0·82	As	−0·53		
Zn	+0·51	Cu($Cu^{\cdot\cdot}$)	−0·58		

The voltage of the Daniell cell with normal solutions is therefore 0·51 − (− 0·58) = 1·09, the copper being positive, since the solution of copper sulphate is negative.

Since ionisation takes place by addition of positive charges to the metal, one metal will dissolve in a solution of another, displacing the latter, when the electrode potential of the former metal is algebraically greater. Thus, if a bar of zinc is placed in a solution of copper sulphate, the zinc tends to throw out ions into the solution. This tendency, in a normal solution of zinc ions, is measured by 0·5 volt. Copper ions, on the contrary, tend to deposit from the solution as metal, since the electrode potential of copper shows that in a normal solution of its ions the metal becomes positively charged, corresponding with deposition of ions. Zinc in a solution of cadmium ions will dissolve, and cadmium will be deposited, since 0·5 − (0·16) = + 0·34; whilst cadmium will deposit copper, since 0·16 − (− 0·58) = + 0·74. Silver will not deposit copper from a solution of copper ions, since − 1·04 − (− 0·58) = − 0·46. These examples show that the electromotive series is an **affinity series.**

Although non-metals are non-conductors, their electrode potentials relative to solutions of their ions may be measured by absorbing a trace of the substance in a platinum plate, and using this as an electrode. A platinum plate immersed partly in chlorine gas and partly in a solution containing chloride ions, say HCl, acts as a chlorine electrode.

Electromotive series of non-metals.

I	−0·78	Cl	−1·50	HSO_4	−2·9
Br	−1·32	OH	−1·96		
O	−1·36	SO_4	−2·2		

Thus, the voltage of the cell: $Zn \mid NZnSO_4 \mid NKBr \mid Br_2,Pt$ will be $0·5 - (-1·32) = +1·82$.

Concentration cells.—Since the electrode potential depends on the concentration of the ions in the solution, two portions of the same metal immersed in two solutions of the same salt, of different concentrations, can form a cell. Cells of this kind are known as **concentration cells.** Their voltage obviously cannot depend on differences of solution pressures, or affinities, since both electrodes and electrolytes are of the same chemical composition. The voltage depends on the fact that copper ions in a concentrated solution of copper sulphate, for instance, tend to deposit on the copper electrode, on account of the greater **osmotic pressure** to a greater extent than copper ions in a dilute solution of copper sulphate. The copper plate in the concentrated solution has a greater positive potential than that in the dilute solutions, since positive ions are driven to it with greater force. The metal dissolves in the dilute solution, and deposits from the concentrated solution, until both solutions become equally concentrated. The combination then shows no voltage.

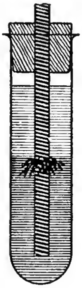


FIG. 413.—Experiment illustrating action of a Concentration Cell.

EXPT. 326.—On a concentrated solution of stannous chloride in a test-tube pour carefully a dilute solution of the same salt. Insert a stick of tin into the liquids, holding it by means of a cork, as shown in Fig. 413. After a few hours a crystalline deposit of tin forms on the rod in the concentrated solution. In this case the current flows through the rod from the concentrated to the dilute solution.

If the electrodes are immersed in solutions which are not of normal concentration with respect to their ions, a correction must be applied to the electrode potentials given in the tables, to take account of the influence of ionic concentration. In more concentrated solutions the osmotic pressures of the ions are more active in tending to cause deposition of the latter on the electrodes. If P_c and P_o are the electrode potentials of a substance in solutions of its ions of concentrations c and 1 gm. equiv. per litre, respectively, then it can be shown that:

$$P_c = P_o + \frac{0·058}{n} \log \frac{1}{c}, \text{ where } n \text{ is the valency of the ion.}$$

Thus, the electrode potential of Zn in a decinormal solution of its ions is $0{\cdot}5 + 0{\cdot}058/2 = 0{\cdot}53$ volt. It is greater than in normal solution, since the opposing osmotic pressure of the ions is less.

The effect of concentration may be very marked. If a solution of potassium cyanide is added to the solution of copper sulphate in the Daniell cell, the copper ions are nearly all removed to form a complex compound, $KCu(CN)_2$, which ionises as $K^{\cdot}$ and $Cu(CN)_2'$, and the direction of the current actually changes sign. On account of the low osmotic pressure of $Cu^{\cdot\cdot}$ ions, copper dissolves and with such ease that zinc ions are driven out of solution as metallic zinc.

Colloids.—It has been stated (p. 12) that the particles of colloids are usually electrically charged. The origin of the electric charge is supposed to be similar to that acquired by metals immersed in liquids, *i.e.*, ions are given off into the solution, and the particles acquire opposite charges. The ions are then attracted to the surface of the colloid particle, and a charged layer is deposited on it. Colloidal metals, for example, send off a few positive ions into the solution, leaving the particles with negative charges. Colloidal ferric hydroxide has the positive charge of the ferric ions which it adsorbs. If water is poured into a glass vessel, the glass sends off sodium ions, charging the liquid positively, and the glass acquires a negative charge. If a solution of copper sulphate is used, sodium ions pass into it, and copper ions are adsorbed by the negative glass surface. If the glass vessel is washed with water, the copper is not removed, but it is dissolved off by acid. A very dilute solution of copper sulphate, which is toxic to sprouted pea-seedlings, is rendered non-toxic by shaking with powdered glass, since the latter adsorbs the copper ions. The charge on colloidal arsenious sulphide is derived from the sulphuretted hydrogen used in its preparation :

$$(As_2S_3)_n + H_2S = H_2S(As_2S_3)_n = H^{\cdot} + HS(As_2S_3)_n'.$$

Oxidation and reduction.—The **oxidation** of stannous chloride to stannic chloride, or ferrous chloride to ferric chloride, by means of chlorine, may be made to furnish an electric current. A cell is made up as follows :

Positive pole : a platinum plate in a solution of a chloride, say NaCl, saturated with chlorine.

Negative pole : a platinum plate immersed in a solution of stannous chloride.

The two are separated by a porous partition. Chlorine dissolves in the platinum, and sends off chloride ions into the solution. The plate is thus left with a positive charge. To neutralise this, negative electrons pass round the wire from the other plate, and the stannous ions which come in contact with this lose negative charges and are oxidised to stannic ions : $Sn^{\cdot\cdot} - 2\epsilon = Sn^{\cdot\cdot\cdot\cdot}$. The current is completed in the cell by chloride ions moving through the porous partition.

Let a cell be constructed as follows :

Negative pole : a platinum plate charged with hydrogen immersed in dilute acid.

Positive pole : a platinum plate in a solution of ferric chloride.

The following action occurs. Hydrogen dissolved in the negative plate throws off hydrogen ions into the solution, leaving the plate charged negatively. The negative charge passes to the other plate, and discharges any $Fe^{\cdot\cdot\cdot}$ ions touching the plate to $Fe^{\cdot\cdot}$ ions. This is a process of **reduction.**

By measuring the voltages of cells of this kind, one can determine the relative **strengths of oxidising and reducing agents.** The following table gives the potentials of oxidising and reducing reagents ; the sign of the potential is that of the solution, as before. The electrodes are platinum plates.

Alkaline $SnCl_2$	$+0{\cdot}30$	KI	$-0{\cdot}89$
Alkaline $NH_2{\cdot}OH$	$+0{\cdot}06$	K_3FeCy_6	$-0{\cdot}98$
H_2	$-0{\cdot}25$	$K_2Cr_2O_7$	$-1{\cdot}06$
$NaHSO_3$	$-0{\cdot}66$	KNO_2	$-1{\cdot}14$
Acid $FeSO_4$	$-0{\cdot}78$	$KMnO_4$	$-1{\cdot}76$

EXERCISES ON CHAPTER XLII

1. Describe with examples how chemical energy may be converted into electrical energy. How is the reverse change effected ?
2. In what units is electrical energy measured ? What are the units of voltage and current, and how are they connected with the unit of energy ?
3. What is meant by total energy and free energy ? How are they connected with the chemical energy change in a reaction ?
4. The voltage of a Weston cell (p. 871) is 1·0186 volts. Find the free energy of the reaction taking place in the cell.
5. What is meant by single potentials and electrolytic solution pressure ? Give an account of the action of the Daniell cell on the basis of Nernst's theory of electrolytic solution pressure.
6. Calculate the voltage of a cell composed of a platinum plate saturated with hydrogen immersed in normal acid as one electrode and a platinum plate in contact with solid iodine in a normal solution of potassium iodide as the other electrode (both electrolytes may be taken as 90 per cent. ionised). Find the free energy of the reaction in the cell, and compare with the heat of formation of hydrogen iodide (p. 410) in solution.
7. How may the oxidising strengths of reagents be compared?

CHAPTER XLIII

THE METALS OF GROUP III OF THE PERIODIC SYSTEM

Group III of the periodic system.—Group III in the periodic table is divided into two parts :

The Boron Sub-group : Boron and the Metals of the Rare Earths.

The Aluminium Sub-group : Aluminium, Gallium, Indium, and Thallium.

All these elements form oxides, R_2O_3, and chlorides, RCl_3. They are generally **tervalent.** Thallium, however, forms univalent, TlX, as well as tervalent, compounds. Boron trioxide is a weakly acidic oxide, but shows feebly basic properties towards very strong acids. The basic character of the oxides increases with the atomic weight. The hydroxides of the aluminium sub-group are amphoteric, forming salts both with strong acids and with strong bases :

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O ; \text{ and}$$
$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O.$$

The metals of the aluminium sub-group do not oxidise very easily in the air, though this tendency increases with the atomic weight. Aluminium is fairly stable in the air, whilst thallium oxidises moderately easily. Aluminium, gallium, and indium form characteristic **alums** with the formula : $\overset{\text{I}}{M}_2SO_4,\overset{\text{III}}{R}_2(SO_4)_3,24H_2O$, which are isomorphous, M being a univalent metal. A true thallium alum has not been prepared.

The element boron, a non-metal, has already been described. The rest of the elements of the group, with the exception of aluminium, are rare, so that they will be described briefly after aluminium.

ALUMINIUM. Al = 26·8.

Aluminium.—Aluminium is the most widely distributed light metal on the surface of the earth. It occurs to the extent of 7·3 per cent. in the earth's crust, as **silicates** in almost all crystalline *silicate rocks* (felspar, augite, hornblende, tourmaline, and micas), and in the secondary formations *clay* ($Al_2O_3,2SiO_2,2H_2O$), and *slate* (clay hardened and laminated by pressure). The **oxide** is found, either anhydrous, as *corundum*, Al_2O_3, or hydrated as *diaspore*,

Al_2O_3,H_2O, *bauxite*, $Al_2O_3,2H_2O$ (amorphous), and *hydrargillite*, $Al_2O_3,3H_2O$. *Felspar*, $KAlSi_3O_8$, or $K_2O,Al_2O_3,6SiO_2$, is a constituent of primary rocks such as granite, and by the disintegration of these rocks, either by simple hydrolysis or by the combined action of moisture and atmospheric carbon dioxide, soluble alkali salts and insoluble hydrated aluminium silicates (clays) pass into the soil :

$$2KAlSi_3O_8 + 3H_2O = Al_2O_3,2SiO_2,2H_2O + 4SiO_2 + 2KOH.$$
$$2KAlSi_3O_8 + 2H_2O + CO_2 = Al_2O_3,2SiO_2,2H_2O + 4SiO_2 + K_2CO_3.$$

The quartz crystals and mica scales of such primary rocks as granite remain *in situ* along with the fine deposit of clay, or *kaolin*, $Al_2O_3,2SiO_2,2H_2O$, derived from the felspar. Any iron present in the rock is oxidised to ferric oxide, which colours the clay yellow or red. The kaolin may be separated from the quartz by washing, when the fine particles of clay are carried away from the larger pieces of quartz. Fine particles of pure clay are separated from a slightly alkaline suspension by cataphoresis (p. 12).

Common clay is contaminated with limestone, quartz, and oxide of iron ; a mixture of clay and limestone constitutes *marl*, whilst a mixture of clay and sand is called *loam*. Nearly all clays contain small amounts of titanium oxide, TiO_2. Aluminium compounds are not absorbed (except in traces) from soils by plants, with the exception of mosses.

Other aluminium minerals are *spinel*, $MgAl_2O_4$, and *chrysoberyl*, $BeAl_2O_4$, in which alumina plays the part of an acidic oxide. *Cryolite*, Na_3AlF_6, is a semi-transparent rock, found in large masses in Greenland. The *turquoise* is a basic aluminium phosphate, coloured blue or green with copper phosphate.

Alum, from which the element takes its name, was probably known to the ancients ; Paracelsus observed that it was not a vitriol (*i.e.*, a compound with a metallic basis), and Pott (1746) showed that it was derived from a peculi . earth, **alumina,** which Marggraf (1754) was first able to isolate from clay. That this earth was the oxide of a metal was regarded as certain by Davy, but the metal, **aluminium** itself, was first isolated by Wöhler in 1827 by the action of sodium on the chloride, $AlCl_3$. Bunsen (1354) prepared aluminium by the electrolysis of the chloride, but the first industrial method of preparation, due to Deville (1854), depended on the reaction used by Wöhler. In 1886 the manufacture of aluminium by the electrolysis of alumina dissolved in fused cryolite was started simultaneously by Hall in America and by Héroult in Europe, where the two processes, differing only in detail, are now used on an extensive scale.

On account of the small chemical equivalent of aluminium (9), and the very high heat of formation of the oxide : $2Al + 3O = Al_2O_3 + 380$

kg. cal., a large expenditure of energy is required, which can be obtained economically only from cheap water power.

The reaction is carried out in the **electric furnace.** The Hall process is worked by the Aluminium Company of America, utilising water power at Niagara, Massena, and Shawinigan Falls. The Héroult process is applied by the Société Electrometallurgique Française, at Froges, and by the British Aluminium Company at Kinlochleven in Scotland.

Manufacture of aluminium.—It has not yet been found possible to produce aluminium from clay ; the source of the metal is *bauxite,* but since this contains iron it is first treated to obtain pure alumina, Al_2O_3.

In Germany, the bauxite is heated to bright redness with sodium carbonate, when **sodium aluminate,** $NaAlO_2$ or Na_2O,Al_2O_3, is produced, alumina being a feebly acidic oxide. The mass is rapidly lixiviated, forming finely-divided oxide of iron, which can be used for the purification of coal gas (p. 682), and a solution of sodium aluminate, from which a granular precipitate of **aluminium hydroxide,** $Al(OH)_3$ or $Al_2O_3,3H_2O$, is thrown down by carbon dioxide at 50–60° : $2NaAlO_2 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3$. On igniting the precipitate, Al_2O_3 is obtained, and the solution of Na_2CO_3 is evaporated and used again. The British Aluminium Co., at Larne (Ireland), uses the **Bayer process.** The bauxite is digested in kiers with caustic soda solution under 80 lb. pressure, giving a solution of sodium aluminate, and leaving oxide of iron, which, however, cannot be used for any purpose. The solution of sodium aluminate is now digested with precipitated alumina, when nearly all the alumina in solution is thrown out as a sandy, amorphous precipitate (β-Al_2O_3), which is easily washed, and on ignition yields pure alumina.

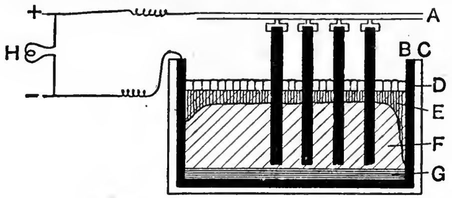


FIG. 414.—Electric Furnace for Aluminium: A. Carbon Anodes; B. Carbon Lining; C. Cast-iron Vessel; D. Carbon Powder Protection; E. Crust of Solidified Electrolyte; F. Molten Electrolyte; G. Molten Metal; H. Low Voltage Charge Control Lamp.

The **electric furnace** consists of an iron box, 6 ft. by 3 ft. by 3 ft., lined with blocks of carbon, which is made the cathode. The anodes consist of rods of petroleum coke or gas-carbon set in a row (Fig. 414) about 2–3 in. above the bottom of the trough. The electrolyte is a solution of alumina (m.-pt. 2010–2050°) in fused cryolite, together with some fluorspar, the temperature being kept at 875–950°.

The eutectic point for a mixture of Al_2O_3, cryolite, and CaF_2 is 868°, and occurs when these are in the proportion 17·7 : 59·3 : 23. In practice, the mixture used is Al_2O_3 10–25, cryolite 90–75, fluorspar 36 per cent. of the cryolite.

The alumina only is electrolysed, the metal (m.-pt. 659°) forming a pool below the anodes, and the oxygen burning the anodes to CO. An E.M.F. of 5–6 volts, and an anodic current density of 100 amp. per sq. dcm., corresponding with a total current of 10,000 amp., are used. The charge is covered with a layer of carbon, and fresh alumina is stirred in from time to time to replace that decomposed. The decomposition is indicated by a rise in resistance, the shunted lamp brightening. About 165,000 tons of aluminium are produced annually in America, France, Great Britain, Canada, Switzerland, Austria, and Germany. The metal has a purity of 99 per cent. Al, the impurities being chiefly iron and silicon.

Properties of aluminium.—Aluminium is a white metal with a blue tinge, the density varying from 2·703 (cast) to 2·709 (rolled). On account of its very small density it has been used in the construction of airships, and engine parts, etc., of motor-cars; the alloy *magnalium* (90–98 Al and 10–2 Mg) is still lighter, and can be worked easily in a lathe, whilst *duralumin* (94·4 Al + 0·95 Mg + 4·5 Cu + 0·76 Mn), sp. gr. 2·77–2·88, can be worked hot or cold, and hardened by quenching from 250–520° in water, the hardness being increased by tempering up to the melting point (520°) after quenching. Duralumin is used in airship construction. Alloys of aluminium with copper are called *aluminium bronzes* (*e.g.*, 90 Cu + 10 Al).

Aluminium melts at 658·5°, and boils at 1800°. Its tensile strength is high: cast 7, sheet 11, wire 13–29 tons per sq. in., that of mild steel being 25. Its surface is unaltered in air, a thin, transparent protecting film of oxide being formed. If this film is removed by rubbing the metal with mercuric chloride, producing a liquid amalgam to which the oxide cannot adhere, rapid oxidation with production of moss-like excrescences of oxide occurs. Amalgamated aluminium foil is also a useful reducing agent, since it reacts in neutral solutions. Aluminium foil or powder readily burns in air with a brilliant flame when heated.

The metal can be cast; at 100–150° it can be wrought, rolled, or drawn, but it becomes brittle at 600°. It is a good conductor of heat and electricity, being used for electric cables in America.

Aluminium can be soldered, but only if a special solder (Al 2·25 + phosphor-tin 0·75 + zinc 17 + tin 80) is used, which is first applied to the metal by heating to 600°, and the two surfaces then pressed together.

About one-thousandth of the weight of aluminium added to molten steel before casting removes oxygen and nitrogen, forming

Al_2O_3 and AlN, and prevents blow-holes in castings. It reacts very violently with silicon steels.

Although only superficially attacked by pure water, aluminium is strongly attacked by sea-water or saline solutions, holes being rapidly formed. Dilute sulphuric acid has very little action on aluminium and the *pure* metal is almost unattacked by dilute or concentrated nitric acid. Dilute and concentrated hydrochloric acids readily dissolve the metal with evolution of hydrogen: $2Al + 6HCl = 2AlCl_3 + 6H_2$. Concentrated sulphuric acid attacks aluminium only when heated:

$$2Al + 6H_2SO_4 = Al_2(SO_4)_3 + 3SO_2 + 6H_2O.$$

The metal readily dissolves in solutions of alkalies, forming **aluminates**: $2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$. These are hydrolysed in solution: $NaAlO_2 + 2H_2O \rightleftharpoons Al(OH)_3 + NaOH$.

The great evolution of heat resulting from the combination of aluminium with oxygen is utilised in **Goldschmidt's thermit process** for reducing metallic oxides (*e.g.*, Cr_2O_3, MnO_2), and for the production of molten steel for welding broken articles (rails, ships' propellers, etc.) *in situ.* A mixture of aluminium powder and oxide of iron ("smithy-scales") is placed in a crucible, and ignited by a magnesium wire (p. 948). A violent reaction occurs: $2Al + Fe_2O_3 = 2Fe + Al_2O_3$, and molten iron, covered with a layer of molten alumina, is formed. The iron is tapped from below directly on to the joint to be welded.

If two plates of aluminium are immersed in sodium bicarbonate solution, and connected with an alternating current supply, the latter is converted into a pulsating direct current. The film of oxide on the metal offers a very high resistance to the current when the plate becomes an anode (+), whilst the metal as a cathode (−) allows the current to pass freely. This arrangement is known as an *aluminium rectifier.* They have been replaced to some extent by thermionic valves (*i.e.*, vacuum tubes with electrodes emitting electrons on heating).

Alumina, Al_2O_3.—**Aluminium trioxide**, or **alumina**, Al_2O_3, is the only oxide of aluminium known with certainty. It occurs native as *corundum*, which forms rhombohedral crystals nearly as hard as the diamond; *emery* is an impure fine-grained variety, used in grinding and polishing. Corundum, when transparent, forms a number of **gems**: *oriental topaz* (yellow); *sapphire* (blue, due to Co, Cr, or Ti oxides); *ruby* (red, due to Cr_2O_3); *oriental amethyst* (violet, due to Mn); *oriental emerald* (green).

Artificial rubies are produced (Verneuil, 1904) by dropping powdered alumina containing 2·5 per cent. of chromium sesquioxide through the centre of an oxyhydrogen flame. The fused mass, or "boule," is caught on a rod of alumina; it is not amorphous, but forms a single crystal, which may be cut. **Artificial sapphires** are made with alumina to which 1·5 per cent. of Fe_3O_4 and 0·5 per cent. of TiO_2 are added ; a reducing flame is used.

Alundum, used as a refractory, is prepared by fusing bauxite in the arc furnace at 2050°, allowing the impurities to settle, cooling, and crushing the upper part. The powder is mixed with a little clay and felspar, moulded, dried, and fired in a porcelain kiln at 1500°. It differs from silica in being a *basic* refractory.

If an alkali is added to a solution of an aluminium salt, *e.g.*, alum, a white, gelatinous precipitate of **aluminium hydroxide**, $Al(OH)_3$, is produced, soluble in excess of potash or soda, but insoluble in ammonia. If this is dried in the air it has the composition : $Al(OH)_3$, or $Al_2O_3,3H_2O$. When dried at 80°, it has approximately the composition $Al_2O_3,2H_2O$. The sandy powder precipitated in Bayer's process (p. 892) has the composition $Al_2O_3,3H_2O$. At 225°, it forms $Al_2O_3,2H_2O$, occurring naturally as *bauxite* (but usually with less water), and at 235° it gives Al_2O_3,H_2O. Al_2O_3,H_2O is also said to be produced by precipitating a *boiling* solution of an aluminium salt with ammonia, and drying at 100°. If these hydrates are heated to dull redness, **alumina**, Al_2O_3, is left as a white powder. Alumina, when calcined at a low temperature, is soluble in acids, but if strongly heated it becomes denser (2·8 at 600°, 3·9 at 1200°), and insoluble in acids. The change appears to take place at 850°, and the product can then be brought into solution only by fusion with caustic soda or potassium bisulphate. In the first case an aluminate, in the second aluminium sulphate, is formed.

Apparently some kind of polymerisation occurs on heating, and the change is probably exothermic. Other oxides, *e.g.*, Cr_2O_3,Fe_2O_3, MgO,TiO_2, undergo more or less sudden exothermic changes at higher temperatures, increasing in density and becoming insoluble in acids, and generally less reactive. In the case of zirconia, ZrO_2, especially, but to a less extent with some of the other oxides, the change is accompanied by incandescence. These changes have been little investigated, since their observation by Berzelius.

Precipitated aluminium hydroxide readily carries down by adsorption various colouring matters and colloidal substances. Hence alum and aluminium salts are largely used as **mordants** in dyeing, and for clarifying water and liquids such as sewage, the calcium carbonate dissolved in which precipitates alumina. In mordanting, the alumina is first precipitated in the fabric, and the latter dipped into the solution of the dye. In clarification, limewater is added to precipitate alumina.

EXPT. 327.—Take two pieces of clean white cotton cloth. Dip one into a solution of aluminium acetate, and dry on the water-bath.

Immerse the two pieces in two beakers, containing boiling solutions of logwood extract; take out after ten minutes and place in beakers of boiling water. The colour is retained by the mordanted fabric, but is leached out of the other. The adsorption product is called a **lake.**

Fabrics are also **waterproofed** by steeping in a solution of aluminium acetate (*q.v.*), and steaming, when colloidal alumina is precipitated in the pores of the fabric ("rainproofs").

Colloidal aluminium hydroxide exists in two forms. (*a*) The precipitated hydroxide is soluble in a solution of aluminium chloride, and the solution on dialysis yields a colloidal aluminium hydroxide, which acts as a mordant, and is coagulated by alkalies or salts, the precipitate being soluble in acids (Graham, 1861). (*b*) If a solution of aluminium acetate is kept for some time at 100° in an open flask, the water which evaporates being replaced, all the acid is expelled, and a second colloidal variety (*meta-aluminium hydroxide*) is formed, which does not act as a mordant; it is precipitated by acids, alkalies, and salts, but the gel is sparingly soluble in acids (Crum, 1854). The gel, dried at 100°, has in each case the composition $Al_2O(OH)_4$. A milky colloidal solution is also formed by the action of 4 per cent. acetic acid on the well-washed precipitated hydroxide.

Aluminium peroxide, Al_2O_4, is precipitated, mixed with alumina, by adding excess of 30 per cent. H_2O_2 to alumina dissolved in 30 per cent. caustic potash solution.

Aluminates.—Aluminium hydroxide readily dissolves in acids, producing **aluminium salts,** and thus acting as a **base**: $Al(OH)_3 + 3HCl \rightleftharpoons AlCl_3 + 3H_2O$. The reaction is reversible, and the salts are hydrolysed by water, indicating that aluminium hydroxide is a weak base. The hydroxide also dissolves in solutions of alkalies, producing **aluminates,** which are extensively hydrolysed by water; it is therefore capable of acting also as a weak **acid.** The acidic properties are weaker than the basic; they are caused by the hydroxyl groups splitting off hydrogen ions. This goes on only in two stages; the normal aluminates, *e.g.*, Na_3AlO_3, apparently do not exist.

$$Al^{\cdot\cdot\cdot} + 3OH' \rightleftharpoons Al(OH)_3 \rightleftharpoons H^{\cdot} + H_2AlO_3' \rightleftharpoons H^{\cdot} + AlO_2' + H_2O.$$

In solution, only the **meta-aluminates,** $RAlO_2$, appear to exist, since the freezing point of a solution of caustic soda is unaltered by dissolved alumina, so that an OH' ion is replaced by AlO_2': $OH' + Al(OH)_3 = AlO_2' + 2H_2O$. If solutions of equal amounts of alumina in acid and alkali, respectively, are mixed, the whole of the alumina is precipitated: $Al^{\cdot\cdot\cdot} + 3AlO_2' = 2Al_2O_3$. Solutions of aluminates are so largely hydrolysed: $NaAlO_2 + 2H_2O \rightleftharpoons NaOH + Al(OH)_3 \rightleftharpoons Na^{\cdot} + OH' + Al(OH)_3$, that they may be titrated with acids as if they were caustic alkalies, and on standing the alumina is slowly deposited. They do not appear to contain colloidal alumina, the slow deposition corresponding with a slow hydrolytic change. When boiled with alumina, all the aluminium hydroxide is precipitated.

Various aluminates occur as minerals, *e.g.*, *spinel*, $MgAl_2O_4$ or MgO,Al_2O_3. The Mg may be replaced isomorphously by Fe (*ous*), Mn (*ous*), Zn, etc., and the Al by Fe (*ic*), Cr (*ic*), Mn (*ic*), etc.—all the minerals being classed as *spinels*. **Cobalt aluminate,** $CoAl_2O_4$, is formed as a blue mass on igniting alumina with cobalt nitrate (blowpipe test for Al), and is known as *Thenard's blue.*

Halogen compounds of aluminium.—Anhydrous **aluminium chloride,** $AlCl_3$, is formed by heating aluminium in hydrogen chloride :

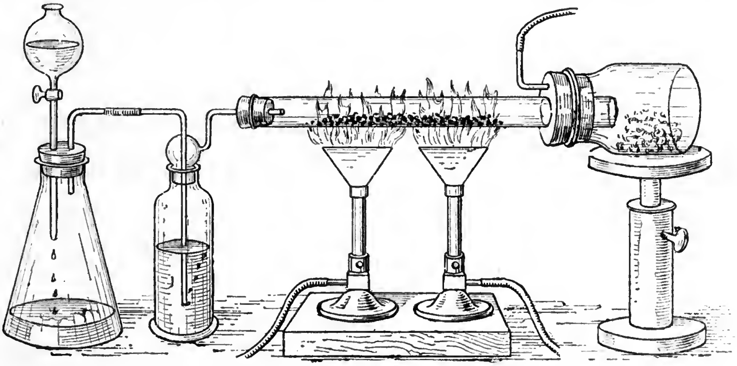


FIG. 415.—Preparation of Aluminium Chloride.

$2Al + 6HCl = 2AlCl_3 + 6H_2$, or by heating strongly a mixture of alumina and carbon in a current of chlorine :

$$\boxed{3Cl_2 + Al_2}\boxed{O_3 + 3C} = 2AlCl_3 + 3CO.$$

Alumina is not decomposed by chlorine, or by carbon alone below 2000° ; the combined affinities of chlorine for aluminium, and of carbon for oxygen, however, bring about the decomposition.

EXPT. 328.—Heat 10 gm. of aluminium turnings in a hard-glass tube connected with a bottle (Fig. 415) and pass over the metal a current of hydrogen chloride dried by sulphuric acid. A sublimate of aluminium chloride is formed, which may be collected in the bottle by heating the tube. When the whole has passed into the bottle, fit a good cork to the latter, as the substance is very hygroscopic.

Anhydrous aluminium chloride is a white, crystalline substance (usually coloured yellow by ferric chloride as impurity), subliming at 183° without previous fusion (m.-pt. 193° under 2 atm. pressure).

The vapour density at 183° corresponds approximately with the formula Al_2Cl_6, but rapidly diminishes with rise of temperature, until at 450° it corresponds with $AlCl_3$, remaining constant at higher temperatures: $Al_2Cl_6 \rightleftharpoons 2AlCl_3$. In organic solvents, the formula is $AlCl_3$; a compound with nitrobenzene has the formula $Al_2Cl_6,C_6H_4NO_2$ in solution in carbon disulphide.

Aluminium chloride fumes in the air, and is very deliquescent. With a little water it forms a crystalline hydrate, $AlCl_3,6H_2O$, which is more conveniently prepared by dissolving aluminium, or alumina, in concentrated hydrochloric acid, and saturating the solution with hydrogen chloride gas. It is hydrolysed in solution: $AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$; the latter has an acid reaction, and can be titrated with alkali as if it were free hydrochloric acid. The anhydrous chloride forms the compounds $AlCl_3,6NH_3$, $AlCl_3,SCl_4$; double salts, *e.g.*, $NaAlCl_4$, are formed by crystallising a mixed solution of the chlorides.

Aluminium bromide, $AlBr_3$, and **iodide,** AlI_3, are formed by passing HBr or HI over heated aluminium. Their properties are as follows:

$AlBr_3$: m.-pt. 93°, b.-pt. 263°; vapour density Al_2Br_6; in solution in CS_2, Al_2Br_6; in nitrobenzene, $AlBr_3$. Forms a crystalline hydrate, $AlBr_3,6H_2O$.

AlI_3: m.-pt. 125°, b.-pt. 350°; vapour density, Al_2I_6; in solution Al_2I_6. Forms crystalline hydrate, $AlI_3,6H_2O$. Reacts with carbon tetrachloride to form CI_4: $4AlI_3 + 3CCl_4 = 4AlCl_3 + 3CI_4$.

Aluminium fluoride, AlF_3, is formed similarly to the chloride, but is much less volatile, and is scarcely soluble in water. Although alumina dissolves in hydrofluoric acid, the solution is strongly supersaturated, and soon deposits the fluoride. Seven hydrates are described. The salt dissolves in hydrofluoric acid, probably forming **hydrofluoaluminic acid,** H_3AlF_6, a salt of which is *cryolite*, Na_3AlF_6, which may contain tervalent fluorine: $Al\vdots(F:FNa)_3$.

Cryolite is used as a flux in the manufacture of aluminium. It has also been used as a source of soda and alumina by **Thomsen's process.** Powdered cryolite (separated from gangue, etc., by electromagnetic processes) is heated with lime: $Na_3AlF_6 + 3CaO = 3CaF_2 + Na_3AlO_3$. The aluminate is dissolved out, and decomposed by carbon dioxide:

$$2Na_3AlO_3 + 3H_2CO_3 = 3Na_2CO_3 + 2Al(OH)_3.$$

Aluminium sulphate, $Al_2(SO_4)_3$.—If alumina is dissolved in hot concentrated sulphuric acid, the liquid on cooling slowly deposits an indistinctly crystalline mass of **aluminium sulphate,** $Al_2(SO_4)_3,18H_2O$. This is purified by redissolving in a little water and adding alcohol. An oily supersaturated solution separates, which soon solidifies to lustrous, scaly crystals of the above formula. On heating the crystals they intumesce, leaving a white mass of anhydrous sulphate, $Al_2(SO_4)_3$. Many other hydrates have been described.

Impure aluminium sulphate is made by heating kaolin (clay) with concentrated sulphuric acid, or bauxite with dilute sulphuric acid. In the first case silica separates:

$$Al_2O_3,2SiO_2,2H_2O + 3H_2SO_4 = Al_2(SO_4)_3 + 2SiO_2 + 5H_2O \, ;$$

the mass is run into moulds, and solidifies. In the second case, the settled solution is evaporated, and the crystals are pressed. The product may contain a considerable amount of ferric sulphate (especially if bauxite is used) which, although it does not form mixed crystals with aluminium sulphate, cannot be separated from it by crystallisation. If the ferric is reduced to a ferrous salt, say by sulphuretted hydrogen, the aluminium sulphate may then be crystallised out alone. The crude mixture, known as *alumino-ferric,* is used for the precipitation of colloidal matter from sewage (p. 895).

If precipitated aluminium hydroxide is dissolved in a solution of aluminium sulphate, a **basic salt** is deposited: $Al_2O_3,2SO_3,xH_2O$. The salt $Al_2(OH)_4SO_4,7H_2O$, or $Al_2O_3,SO_3,9H_2O$, occurs as *websterite,* used in the preparation of alum.

Alums.—The name **alum** was given originally to a double salt of aluminium sulphate and ammonium sulphate,

$$(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O,$$

which readily crystallises in octahedra. It was prepared from *alum shale, i.e.,* aluminium silicate permeated by pyrites, FeS_2, which on roasting in heaps forms a mixture of aluminium and ferric sulphates. The roasted shale is lixiviated, and after evaporation, either ammonium sulphate (originally ammonium carbonate, *i.e.,* stale urine), or potassium sulphate or chloride, added. The alum is deposited. Potash alum is prepared from *alunite,* or alum-stone, $K_2SO_4,Al_2(SO_4)_3,4Al(OH)_3$, by heating to 500–600°, digesting with concentrated sulphuric acid, and adding potassium sulphate. Alum is now usually made by adding the alkali-sulphate to a solution of alumino-ferric. Since alum is readily purified by recrystallisation, it may be obtained free from iron (which gives dull colours to lakes in mordanting) very much more readily than aluminium sulphate. Alum prepared from alunite, called *Roman alum,* is quite free from iron.

If caustic potash is added to a solution of alum, the precipitate of alumina at first redissolves on stirring, but at a certain point a permanent precipitate begins to form. The crystals deposited from this solution on heating to 40° are known as **neutral alum** and are identical in composition with alunite. They redissolve on cooling. If a little alkali is added to a solution of alum, the latter, on evaporation, separates in *cubes*. Potash-alum appears to effloresce in air; in reality ammonia is absorbed from the atmosphere, and a basic salt is formed.

Potash-alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, when heated melts at 92°, and loses the whole of its water at 200°, forming a white, porous mass of **burnt alum.** **Ammonia-alum** on the other hand, which melts at 95°, loses ammonia and sulphuric acid as well, and on ignition leaves a residue of pure alumina:

$$(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O = 2NH_3 + 4H_2SO_4 + Al_2O_3 + 21H_2O.$$

The name **alum** is given to all double-salts of the type

$$\overset{\mathrm{I}}{R}_2SO_4,\overset{\mathrm{III}}{M}_2(SO_4)_3,24H_2O.$$

$\overset{\mathrm{I}}{R}$ may be K, NH_4, Na, Cs, $\overset{\mathrm{I}}{Tl}$, hydroxylamine, or the radical of an organic quaternary nitrogen base, such as $N(CH_3)_4$. (Li gives no alum.) M may be Al, $\overset{\mathrm{III}}{Fe}$, $\overset{\mathrm{III}}{Cr}$, $\overset{\mathrm{III}}{Mn}$, $\overset{\mathrm{III}}{In}$, $\overset{\mathrm{III}}{Tl}$, Ga, $\overset{\mathrm{III}}{V}$, $\overset{\mathrm{III}}{Co}$, $\overset{\mathrm{III}}{Ti}$, $\overset{\mathrm{III}}{Mn}$, $\overset{\mathrm{III}}{Rh}$, etc. The radical SeO_4 of selenates may replace SO_4. An alum containing uni- and ter-valent thallium together does not exist, although $\overset{\mathrm{I}}{Tl}_2SO_4,\overset{\mathrm{III}}{Al}_2(SO_4)_3,24H_2O$ exists, and ammonium alum containing thallic sulphate, in mixed crystals, is known. All the alums are isomorphous, form mixed crystals in all proportions, and also "layer-crystals," *i.e.*, a crystal of any one alum continues to grow in a solution of any other. The sodium alum is very soluble, and its preparation is difficult.

Aluminium sulphide, Al_2S_3, is formed from its elements, or by passing sulphur vapour over a heated mixture of alumina and carbon. It is *completcly* hydrolysed by water: $Al_2S_3 + 3H_2O = 2Al(OH)_3 + 3H_2S$, and is not formed by adding ammonium sulphide to a salt of aluminium; in this case aluminium hydroxide is precipitated, and sulphuretted hydrogen evolved: $Al^{\cdots} + 3HS' + 3H_2O = Al(OH)_3 + 3H_2S$ (*cf.* Cr, p. 953).

Aluminium nitride.—Aluminium combines directly with nitrogen at 740°, forming the **nitride**, AlN, in small yellow crystals, or as a bluish-green powder. The impure nitride is formed by heating a mixture of bauxite and carbon to 1600° in a current of nitrogen: $2Al_2O_3 + 6C + 2N_2 = 4AlN + 6CO$. At 1850°, the nitride decomposes. When the impure nitride is heated in a carbon tube at 2020° in a stream of nitrogen, colourless hexagonal needles of pure nitride are formed. Aluminium nitride is decomposed by hot dilute alkali, with evolution of ammonia: $2AlN + 3H_2O = Al_2O_3 + 2NH_3$. This is the Serpek process, formerly used for the fixation of atmospheric nitrogen.

Aluminium nitrate, $Al(NO_3)_3,18H_2O$, is prepared by mixing solutions of aluminium sulphate and lead nitrate, filtering, and evaporating. Other crystalline hydrates (15, 16, or $12H_2O$) are known. A solution of the salt is used as a mordant. **Aluminium acetate,** $Al(C_2H_3O_2)_3$, is obtained from lead acetate and aluminium sulphate.

Ceramics.—The manufacture of *porcelain,* carried out by the early Chinese and Egyptians, remained a lost art in Europe until 1709, when it was rediscovered by Böttcher; in 1710 the famous Meissen works in Saxony was started. After 30,000 experiments, Pott, in Prussia, also rediscovered the secret, and the Berlin works was begun. The process was rediscovered in France, chiefly owing to the work of Réaumur, about 1758, and the Sèvres works was established in 1767. The earlier work of Bernard Palissy (1509–1589) was directed mainly to the glazing and colouring of pottery, or earthenware, as distinct from porcelain.

The production of pottery (which was carried to a high stage of perfection by the Etruscans) and of porcelain depends on the changes produced in **clay** by heating (or "firing"). Pure clay (*kaolinite*) has the formula $Al_2O_3,2SiO_2,2H_2O$. On heating, moisture is first driven off and colloidal matter coagulated. At 500°, the kaolinite decomposes: $Al_2O_3,2SiO_2,2H_2O = Al_2O_3 + 2SiO_2 + 2H_2O$ (or $Al_2O_3,2SiO_2 + 2H_2O$); at 800°, the alumina begins to polymerise, and the mass shrinks; above 1000°, combination occurs between alumina and silica, with formation of *sillimanite,* Al_2O_3,SiO_2; at 1500° (the temperature of firing porcelain), this sinters to a stony mass, which softens at 1650°, and at 1700° fuses to a brown or grey viscous liquid.

In order to separate from clay the oxide of iron which discolours the product, Schwerin mixes clay with water and dips in electrodes. The clay particles wander to the anode, the oxide of iron to the cathode. The clay behaves in some ways like a colloid; brick clay becomes much more plastic if mixed with a little dilute alkali, which appears to give charges to the clay particles, causing them to repel one another. In ordinary brickmaking, the clay is kneaded with water and allowed to stand, when organic colloids (humic acids), conferring plasticity, appear to be formed. (An infusion of straw has the same effect.) Clay used in making pottery is washed, and the coarse particles are allowed to settle. The fine clay is then allowed to deposit, and excess of water removed by air drying. It is then highly plastic, and can be worked on the wheel. The goods are air dried by stacking in warmed rooms, and then burnt in clay boxes, called *seggars,* stacked in a kiln. The product, which has undergone shrinkage, is called *biscuit* or *earthenware.* In treating porcelain clay, the mass is sterilised before working up, as further fermentation would develop bubbles. In the Berlin porcelain works the sterilisation is effected by exposure to ultraviolet light.

Bricks are made from impure clay, containing sand and oxide of iron, which gives them a red colour after firing at about 950°. The yellow bricks used in the South of England are made from mixtures of clay and chalk. Purer clay is used for *earthenware*, which is fired at a higher temperature: 1–3 per cent. of Fe_2O_3 forms a buff-coloured product; 4–5 per cent. a red. *Porcelain* is made from a mixture of the purest China-clay, or *kaolin*, free from iron, with a material containing silica. Thus, Berlin porcelain is made from 55 parts of kaolin, 22·5 of pure quartz, and 22·5 of felspar. It is fired at about 900°, then the glaze is put on, and the goods are fired at a bluish-white heat (1400–1500°). The temperature is regulated by pyrometers, or by small clay cones (*Seger cones*), which soften and bend over at particular temperatures in the furnace. The mass undergoes partial fusion and the resulting product is translucent.

In the process of firing clay, the particles at the highest temperature undergo partial fusion and become cemented together, forming a stony mass. Clay containing a large proportion of silica and alumina in comparison with the basic oxides (Na_2O,CaO) always present as impurities, is very refractory, and is called *fireclay* (*e.g.*, Stourbridge clay). This is made into refractory bricks, and to prevent undue contraction on firing, broken firebricks ("grog") are added to the clay before heating. Graphite may also be incorporated with the fireclay when it is formed into crucibles.

The clay after firing forms the *body* of the ceramic; this is called *biscuit* if porcelain clay is used; otherwise it is called *earthenware*. It is next glazed. The **glaze** is a glassy surface imparted to the body, and intimately united with it. Earthenware drainpipes and cheaper goods are often **salt-glazed**; common salt is thrown into the kiln and is vaporised at the high temperature, forming a thin layer of fusible silicate on the surface of the ware. Salt-glazed ware is suitable for pipes for conveying acids. Table-ware is usually **lead-glazed**: the ware is dipped into a creamy paste of a mixture of 60 parts of lead oxide, 10 of clay, and 20 of ground flints. Some of this adheres to the surface, and is fused in the furnace to a glass. **Porcelain** is glazed by dipping and re-firing, as in the case of earthenware. The glaze may be ground felspar, or mixtures; *e.g.*, *Berlin glaze* consists of: kaolin 31, quartz 43, gypsum 14, and broken porcelain, 12.

The ware may be *painted* before glazing (some colours are applied on the glaze); the colours are metallic oxides (*e.g.*, cobalt oxide), which form coloured glasses (p. 850) with the glaze, or with lead oxide and silica, or borax, applied with the colouring oxide, before the glaze is applied. In porcelain used in laboratories the glaze must adhere firmly to the body, and the thermal expansions be so adjusted that no tendency to separation occurs on heating. Berlin porcelain is well known for its excellence in these respects. *English bone chin* contains 30–50 per cent. of bone-ash (calcium phosphate). It is less resistant than Berlin ware.

The following table contains a **classification of ceramic products**:

- I. Porous body, permeable to water:
  - (1) *Unglazed*
    - (*a*) softens above 1400° (*non-refractory*)—*terra cotta*;
    - (*b*) does not soften above 1400° (*refractory*)—*firebrick, refractory ware.*
  - (2) *Glazed*
    - (*a*) *fine earthenware* (white body);
    - (*b*) *sanitary ware* (fireclay body);
    - (*c*) *faience* (coloured body, white glaze): first made in Faenze (Italy); rediscovered by Bernard Palissy;
    - (*d*) *Majolica* (enamelled faience), first made in Majorca.
- II. Non-porous body, impermeable to water:
  - (*a*) translucent: *porcelain*;
  - (*b*) opaque: *stoneware.*

Crucibles are made from a pure clay mixed with coarse sand or ground burnt clay. The most refractory kinds contain the largest proportion of silica. A mixture of clay and graphite is also used.

Ultramarine.—The rare mineral *lapis lazuli*, which has a beautiful blue colour, is a sodium-aluminium silicate containing sulphur in some form not completely defined, but probably as sodium sulphide. Ancient Egyptian amulets of this stone (which is very soft) are common. In 1828, Gmelin obtained artificial *lapis lazuli*, or **ultramarine,** by heating clay with sodium sulphate and carbon.

A mixture of 100 parts of kaolin, 70 of soda-ash, 80 of sulphur, and 14 of resin is heated to bright redness in a closed crucible. A **white ultramarine,** with the approximate composition $Na_7Al_3Si_3S_2O_{12}$, is formed. If air is admitted during heating, a **green ultramarine,** $Na_5Al_3Si_3S_2O_{12}$, is formed. If this, or white ultramarine, is mixed with powdered sulphur, and heated in air, **blue ultramarine,** $Na_4Al_3Si_3S_2O_{12}$, is formed, which is ground and washed. If this, which is the commercial product, is heated in a stream of dry chlorine, nitric oxide, or hydrogen chloride, a **violet.** and finally a **red, ultramarine** result. The cause of the colours is not clear: it has been suggested that colloidal sulphur is present.

Alkalies are without action on ultramarine, so that it can be used in laundering to give a white appearance to linen, as it is not attacked by soap or soda. Acids, however, rapidly decompose it, with evolution of sulphuretted hydrogen and a white, gelatinous residue remains. Fuming sulphuric acid does not produce this change. The sodium in ultramarine may be replaced by its equivalent of silver by treatment with silver nitrate, and a brown **silver ultramarine** obtained. Potassium and lithium chlorides give, with silver ultramarine, corresponding potassium and lithium ultramarines.

GALLIUM (Ga = 69·5), AND INDIUM (In = 113·9).

Gallium and Indium.—The rare element **gallium** (Ga = 69·5) occurs in minute traces in most specimens of zinc blende, and was discovered by the spectroscope in a blende from Pierrefitte by Lecoq de Boisbaudran in 1875. It is the *eka-aluminium* of Mendeléeff (p. 470). Gallium occurs in traces in bauxite, and in commercial aluminium. Middlesbrough cast-iron contains 1 part of gallium in 33,000. Gallium fuses at 30·1° and remains supercooled, so that it is often considered as a liquid element, along with mercury and bromine. **Indium,** In = 113·9, was discovered by Reich and Richter in the spectroscopic examination of zinc blende from Freiburg (1863). It gives a dark blue flame coloration. The oxide is In_2O_3, but three chlorides, InCl, $InCl_2$, and $InCl_3$, are known, with normal vapour densities. Indium and gallium form **alums,** $K_2SO_4,\overset{III}{R}_2(SO_4)_3,24H_2O$

THALLIUM. Tl = 202·4.

Thallium.—In 1861, Crookes observed a bright green line in the spectrum of a specimen of flue dust from a vitriol works, which he found was due to the presence of a new metal. The element was independently discovered a year later by Lamy. Crookes gave it the name **thallium,** from the Greek *thallos*, a young twig, on account of the colour imparted to the flame. The only minerals rich in thallium are *crookesite* (17 per cent. Tl, with Se, Cu, Ag), and *lorandite*, $TlAsS_2$.

Thallium may be obtained from vitriol flue-dust, or from pyrites (from which it passes into the flue-dust), by dissolving in *aqua regia*, evaporating, precipitating with sulphuretted hydrogen and then ammonia in the usual group separations, and then adding potassium iodide to the filtrate. A yellow precipitate of **thallous iodide,** TlI, is formed, which gives a green coloration when heated on platinum wire in a Bunsen flame. If this is reduced with zinc and dilute sulphuric acid the **metal** is obtained. Thallium is a soft, greyish-white metal, m.-pt. 303°; its vapour density corresponds with the formula Tl_2. It oxidises in moist air, decomposes steam at a red-heat, and dissolves readily in dilute sulphuric, and especially in nitric, acid. It is less easily soluble in hydrochloric acid, since thallous chloride, TlCl, is sparingly soluble.

Thallium forms two series of compounds: the **thallous compounds,** RX, in which it is univalent and shows analogies with silver and the alkali-metals; and the **thallic compounds,** RX_3, in which it is tervalent, and exhibits resemblances to aluminium.

If thallium is dissolved in dilute sulphuric acid and the solution evaporated, **thallous sulphate,** Tl_2SO_4, isomorphous with potassium sulphate, and forming an **alum,** $Tl_2SO_4,Al_2(SO_4)_3,24H_2O$, is obtained. From its solution, hydrochloric acid precipitates white **thallous chloride,** $TlCl$, resembling silver chloride in becoming violet on exposure to light, but differing from silver chloride in being sparingly soluble in ammonia. With chloroplatinic acid a sparingly soluble **chloroplatinate,** Tl_2PtCl_6, resembling K_2PtCl_6, is formed. Iodides precipitate yellow **thallous iodide,** TlI, almost insoluble in cold water, but dissolving in 800 parts of boiling water (*cf.* PbI_2).

Thallous hydroxide, $TlOH,H_2O$, is obtained in yellow needles by decomposing a solution of thallous sulphate with baryta-water and evaporating. The solution turns turmeric paper brown, and is therefore alkaline (*cf.* KOH), but then bleaches it. If heated out of contact with air at 100°, TlOH forms black **thallous oxide,** Tl_2O, dissolving in water to form a colourless solution of TlOH. On addition of bromine and alkali, this solution gives a brown precipitate of **thallic hydroxide,** $Tl(OH)_3$, or $TlO(OH)$, which loses water on heating and forms reddish-brown **thallic oxide,** Tl_2O_3. This evolves chlorine with hydrochloric acid, and forms TlCl (*cf.* Pb_2O_3).

Sulphuretted hydrogen throws down a black precipitate of **thallous sulphide,** Tl_2S, from alkaline solutions of thallous salts. It is soluble in dilute acids (except acetic), but insoluble in ammonium sulphide.

Thallous hydroxide solution absorbs carbon dioxide, forming the soluble **thallous carbonate,** Tl_2CO_3, the solution of which is hydrolysed (*cf.* K_2CO_3).

Thallic chloride, $TlCl_3,4H_2O$, is formed by passing chlorine through thallous chloride suspended in water, and evaporating at 60°. **Thallic sulphide,** Tl_2S_3, is a black pitch-like mass, obtained by fusing thallium with excess of sulphur. **Thallic sulphate,** $Tl_2(SO_4)_3,7H_2O$, is formed by dissolving thallic oxide in dilute sulphuric acid; it is decomposed by water with precipitation of a basic salt, $Tl(OH)SO_4,2H_2O$, and forms with potassium sulphate a compound $K_2SO_4,Tl_2(SO_4)_3,8H_2O$, which is not a true alum.

In its analogies to the alkali-metals, lead, and aluminium, thallium shows a greater diversity of properties than most other elements: Dumas appropriately called it the "ornithorhynchus amongst the metals"—the duckbill platypus.

Thallium is used to a limited extent in the production of a very refractive optical glass, obtained by fusing the carbonate with sand and red lead.

An oxide, TlO, is obtained as a black precipitate by the action of hydrogen peroxide on an alkaline solution of thallous sulphate; its formula is considered to be Tl·O·Tl:O. Another oxide, Tl_3O_5, is said to be deposited on the anode in the electrolysis of a solution of Tl_2SO_4 faintly acidified with oxalic acid.

THE RARE EARTHS.

The rare earths.—The substances known as the **rare earths** are the oxides of metals which, with the exception of **cerium,** belong to the third group of the Periodic System. Their general formula is thus R_2O_3; the most stable cerium oxide, however, is CeO_2. They occur in rare minerals found in Scandinavia, Siberia, Greenland, North America, and Brazil, usually in the form of silicates. Not only are some of these elements present in small amounts in the crust of the earth, but they differ from such rare elements as lithium, which are widely diffused, in occurring solely in a few special localities. Their compounds are therefore (with the exception of those of cerium) very expensive and were, until the fairly recent discovery of the monazite deposits of Brazil and Carolina, in the hands of a very limited number of chemists. The properties of many members of this group of elements are consequently imperfectly known. In addition to this, the different elements resemble one another so closely, and are separated only with such great difficulty, that many substances formerly thought to be definite chemical individuals have on further investigation proved to be mixtures, and in many cases the individuality of some of the rare earths is still a matter of doubt. Crookes, to whom much of the pioneering work on this group of elements is due, concluded in 1887 that the elements contained in the rare earths might be mixtures of closely related elements, the atomic weights of which were very near together. He called these **meta-elements,** and supposed that many of the ordinary chemical elements might be of similar constitution. Improved methods of separation of the rare earths have not confirmed Crookes's hypothesis, and the recent work on the *X*-ray spectra of the rare earths (p. 1030) has placed their individuality on a more satisfactory basis.

As an example of the difficulties encountered in this branch of chemistry, reference may be made to the separation of an earth called "didymia," regarded as a pure substance by Lecoq de Boisbaudran (1879), into two new earths, **neodymia** and **praseodymia,** by Welsbach in 1885. The "didymium" salts were colourless, but in solution exhibited an absorption spectrum in the green and red. By repeated crystallisation of the nitrates from nitric acid, two fractions were obtained, one green (praseodymium salt) and the other rose-coloured (neodymium salt), showing separately the two parts of the absorption spectrum of the original substance. The colours are complementary, and the mixture, as in the case of a mixture of cobalt and nickel salts, is colourless. Since neodymia and praseodymia always occur with the other earths, the absorption bands in the spectrum, even of light reflected from the sand or native earth, is an indication of the presence of rare earths.

The rare earths exhibit very beautiful phosphorescent effects on exposure to cathode rays in vacuum tubes, and **phosphorescence spectra** obtained in this way were studied by Crookes. It has been found, however, that the pure earths are not phosphorescent, but show the effect only in presence of small amounts of other substances, so that the importance once attached to these spectra has receded.

Rare earth minerals.—Minerals containing the rare earths occur in relatively few localities, and each mineral usually contains a number of the earths. Cerite contains lanthanum, praseodymium, neodymium, and samarium, in addition to cerium, and also traces of other earths: gadolinite contains chiefly yttrium, erbium, etc., with only small amounts of cerium and lanthanum. The rare earths are therefore usually divided into two groups:

I. **Cerite earths**: oxides of cerium, lanthanum, praseodymium, neodymium, samarium, and europium.

II. **Gadolinite earths**: oxides of gadolinium, scandium, yttrium, terbium, dysprosium, erbium, thulium, and lutecium.

The earths called celtia, phillipia, mosandria, decipia, and victoria have been proved to be mixtures of the above. Examples of rare earth minerals are the following: cerite, $H_3(Ca,Fe)Ce_3Si_3O_{13}$; orthite, $AlOHCa_2(Al,Fe,Ce)_2(SiO_4)_3$; gadolinite, $(Fe,Be)_2Y_2Si_2O_{10}$; xenotine, YPO_4; fergusonite, $YNbO_4$; Australian fergusonite, $YTaO_4$; columbite and tantalite, $[(Nb,Ta)O_3]_2(Fe,Mn)$; euxenite, polycras, blomstrandite, and priorite, containing Nb, Ta, and Ti; samarskite, containing U, Th, Nb, Ta; microlith, $Ca_2(Ta,Nb)_2O_7$; yttrotantalite, $Y_4(Ta_2O_7)_3$.

Separation of the rare earths.—The rare earths are precipitated by oxalic acid from *acid* solutions. The different earths so obtained are then separated by one or more of the following processes:—

(1) Fractional decomposition of the nitrates by ignition.

(2) Fractional precipitation with a base.

(3) Fractional crystallisation of salts and double salts, *e.g.*, with ammonium nitrate, bismuth nitrate, etc.

(4) Fractional precipitation of salts with oxalic acid, succinic acid, sodium stearate, etc.

A separation, *e.g.*, by fractional crystallisation, may be represented diagrammatically by Fig. 416, and from this the tedious character of the operation may be inferred. Many hundreds of fractions may be necessary to attain separation. In the diagram, the less soluble constituent may be considered as accumulating on the right hand side.

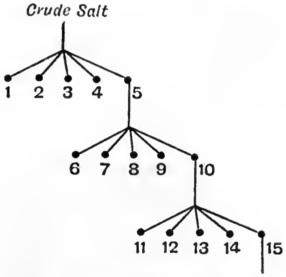


FIG. 416.—Diagram illustrating Separation of Rare Earths.

Cerium, Ce = 139·15.—The only rare earth element of importance is **cerium,** compounds of which are produced in relatively large amounts in the preparation of thorium salts from monazite (p. 930). By the electrolysis of the chlorides of these elements, impure metallic cerium (containing lanthanum and other rare earth elements), which is known as "Mischmetall," is obtained. This is alloyed with iron, and used in automatic lighters, since when it is abraded with steel it throws off very hot sparks which will ignite coal gas, or the vapours of alcohol and petrol.

Cerium forms **two series of compounds**, viz., the **cerous salts,** $\overset{\text{III}}{\text{Ce}}\text{X}_3$; and the **ceric salts,** $\overset{\text{IV}}{\text{Ce}}\text{X}_4$. The cerous salts, in which the element is tervalent, are stable and colourless, usually similar in composition and isomorphous with the corresponding compounds of other rare earth elements. If, however, cerous salts with volatile acids (oxalate, nitrate) are heated, the oxide remaining is not cerous oxide, Ce_2O_3, corresponding with the rare earths, but **cerium dioxide,** CeO_2, which is the stable oxide and is known as *ceria*. **Cerous oxide,** Ce_2O_3, is obtained by reduction of the dioxide with calcium. **Cerous hydroxide,** $Ce(OH)_3$, which is formed as a white precipitate on addition of alkalies to solutions of cerous salts, is rapidly oxidised on exposure to air, becoming red and violet, and finally pure yellow when **ceric hydroxide,** $Ce(OH)_4$, is produced. The latter is obtained by adding sodium hypochlorite and alkali to a solution of a cerous salt.

Cerium dioxide, or **ceria,** CeO_2, obtained by heating the oxalate, is a nearly white powder with a faint yellow tinge. If traces of praseodymium salts are present, the oxide is darker in colour, and 1 per cent. of Pr_2O_3 communicates to ceria a dark brown colour. The commercial oxide is usually yellowish-brown. Ceria when treated with hot concentrated sulphuric acid forms yellow **ceric sulphate,** $Ce(SO_4)_2$, which is a powerful oxidising agent and dissolves in water to form a yellow solution. The solution is reduced, with evolution of oxygen, by hydrogen peroxide, a colourless solution of **cerous sulphate,** $Ce_2(SO_4)_3$, being formed. This gives a characteristic double salt with potassium sulphate, $Ce_2(SO_4)_3,K_2SO_4,3H_2O$, which is insoluble in a solution of potassium sulphate, and is used in the separation of cerium. **Cerous oxalate**, $Ce_2(C_2O_4)_3,10H_2O$, is precipitated from solutions of cerous salts by oxalic acid.

Ceria dissolves with difficulty in concentrated hydrochloric acid, forming a dark brown unstable solution of **ceric chloride**, $CeCl_4$, which on heating evolves chlorine and leaves a solution of **cerous chloride**, $CeCl_3$. This is obtained anhydrous as a yellowish-white sublimate when a mixture of ceria and carbon is heated in chlorine.

Ceric salts are hydrolysed by water, basic salts being precipitated. The most stable are the double nitrates with alkali metals, $R_2Ce(NO_3)_6$, which crystallise well, are soluble in water and alcohol, and are bright red in colour.

If ceria is heated in hydrogen, a dark blue **suboxide**, Ce_4O_7, is formed, which smoulders when heated in air, forming CeO_2. A **hydride**, CeH_3, is formed as a dark blue powder when hydrogen is passed over cerium at 250–270°. It ignites spontaneously in air.

Cerous salts are **oxidised** to ceric salts by potassium permanganate in neutral or slightly alkaline solution, by ammonium persulphate in hot dilute solutions containing a little persulphuric acid, or by anodic oxidation in electrolysis. Ceric salts are **reduced** to cerous salts by electrolytic reduction, by prolonged boiling with concentrated hydrochloric acid, or more rapidly by hydrochloric acid and stannous chloride. **Cerous salts** in alkaline solution are reducing agents: they precipitate cuprous oxide from Fehling's solution: $2CuO + Ce_2O_3 = Cu_2O + 2CeO_2$, and mercurous oxide from mercuric chloride: $2HgO + Ce_2O_3 = Hg_2O + 2CeO_2$. Gold and silver are precipitated as metals. In this reducing action they differ from the salts of all the other rare earths.

In alkaline solution, cerium salts are oxidised by hydrogen peroxide to a reddish-brown hydrated **peroxide**:

$$Ce(OH)_4 + H(O_2H) = Ce(O_2H)\,(OH)_3 + H_2O.$$

If potassium carbonate and then H_2O_2 are added to a neutral solution of a cerous salt, and the liquid is warmed to 40–60°, a yellow colour due to cerium peroxide is formed. This is a delicate test for cerium.

	Ce.	La.	Nd.	Pr.	Sa.
Specific gravity	7·0242	6·1545	6·9563	6·4745	7·7–7·8
Melting point	623°	810°	840°	940°	1300°–1400°
Heat of combustion	1·603	1·602	1·506	1·467 kgm.cal.per gm.	
Specific heat	0·04479	0·04485	—	—	—

EXERCISES ON CHAPTER XLIII

1. How is alum prepared ? What chemical compounds are known as "alums" ?

2. In what forms does aluminium occur in Nature ? How is the metal manufactured, and for what purposes is it used ?

3. For what purposes are aluminium salts used ? Describe the preparation of (*a*) aluminium sulphate from kaolin, (*b*) anhydrous aluminium chloride from aluminium. What is the molecular weight of the chloride ?

4. How are aluminates obtained ? Describe reactions in which alumina functions as an acidic and as a basic oxide.

5. How is porcelain made ? What varieties of ceramic products are manufactured ?

6. Where do gallium, indium, and thallium occur ? How were these elements discovered ?

7. How may a thallium salt be obtained from iron pyrites containing this element ? What elements does thallium resemble ? Discuss its position in the Periodic System.

8. What are the "rare earths" ? How are they separated from one another, and for what purposes are any of them used ? Discuss the position of cerium in the classification of the elements.

CHAPTER XLIV

THE METALS OF THE FOURTH GROUP

The carbon group—Group IV in the Periodic System, often called the **Carbon group**, contains two non-metals, carbon and silicon, and seven metals. The two sub-groups are :

Odd series :

Germanium, Ge = 71·9, m.-pt. 960°, sp. gr. 5·47.
Tin, Sn = 117·8, m.-pt. 232°, sp. gr. 7·29.
Lead, Pb = 205·55, m.-pt. 327°, sp. gr. 11·35.

Even series :

Carbon, C = 11·91, m.-pt. 7360°.
Silicon, Si = 28·1, m.-pt. 1420°, sp. gr. 2·49.
Titanium, T = 47·72, m.-pt. 1800–1850°, sp. gr. 4·87.
Zirconium, Zr = 89·9, m.-pt. 1530°, sp. gr. 4·08.
(**Cerium, Ce** = 139·15, m.-pt. 623°, sp. gr. 7·0).
Thorium, Th = 230·31, m.-pt. 1700°, sp. gr. 11·0.

Of these metals all but two, tin and lead, are rare. Cerium, although forming compounds of the type CeX_4, typical of the group, is more conveniently described with the rare earths (Chapter XLIII.). In Group IV, the differences between the odd and even series are very ill-defined. The **electrochemical characters** of the elements are also not pronounced, because the group forms the transition between the electropositive (base-forming) elements of group III, such as aluminium and the metals of the rare earths, and the electronegative (acid-forming) elements of the succeeding group V, such as nitrogen and phosphorus.

The two non-metals of the group are fusible only with the greatest difficulty ; the metals also, with the exception of tin and lead, have high melting points. Carbon, silicon, germanium, zirconium, and thorium, form **hydrides**, RH_4. All the elements of the group form

chlorides, RCl_4, although in the case of lead the stable chloride is $PbCl_2$:

$SiCl_4$, b.-pt. 57·5° ; $SiHCl_3$, b.-pt. 34°.
$GeCl_4$, b.-pt. 86° ; $GeHCl_3$, b.-pt. 75°.
$SnCl_4$, b-pt. 114·1°.
$PbCl_4$, decomposes.

CCl_4, b.-pt. 76·7° ; $CHCl_3$, b.-pt. 61·2°.
$TiCl_4$, decomposes.
$ZrCl_4$, sublimes.
$CeCl_4$, stable only in solution.
$ThCl_4$, m.-pt. 8·20° ; sublimes.

Especially characteristic of the group are the compounds $RHCl_3$, known as **chloroforms.**

The typical **oxides**, RO_2, are all known. Numerous other compounds besides those corresponding with the type RX_4 are formed by the elements. In the cases of C, Si, Ge, Ti, Zr, Th, RX_4 is the stable type ; Sn and Pb form stable compounds of the type RX_2 ; in the case of lead, the only *stable* compounds of the quadrivalent type are the dioxide, PbO_2, and some double compounds. Cerium also forms compounds of the type RX_3, and on the whole shows close analogies to elements of the preceding group. In many of its chemical properties lead shows close analogies to barium, in the second group ; *e.g.*, its sulphate, $PbSO_4$, is very sparingly soluble in water and is isomorphous with $BaSO_4$, with which it often occurs in the ores.

The element **carbon** differs from all the other elements in the number of its compounds. The study of these constitutes a special branch of chemistry—organic chemistry (p. 658).

TIN. Sn = 117·8.

Tin.—Although it is supposed that the word *bedil* in the Old Testament refers to tin, the metal was first distinctly mentioned by Pliny, who speaks of *plumbum nigrum* (lead), and *plumbum candidum* (tin), observing that the latter was brought from the Islands of Cassiterides, in the Atlantic. This undoubtedly refers to the British Isles, and the island Iktis, on the coast of Britain, which (according to Diodorus Siculus) was separated from the mainland only at high water, is no doubt St. Michael's Mount, Cornwall, where tin ore is found. The metal was afterwards given the Latin name *stannum*. The Latin Geber refers to the curious crackling noise, or " cry of tin," resulting when a bar of tin is bent ; this is due to the friction of the crystalline particles. The alchemists associated tin with the planet Jupiter, giving it the symbol ♃ : the thunderbolt of Jove.

Tin occurs in small quantities in Siberia, Guiana, and Bolivia in the metallic state ; its commonest ore is *tinstone*, or *cassiterite*, the **dioxide,** SnO_2 (m.-pt. 1127°), which is found in large quantities in Devon and Cornwall, the Straits Settlement, Saxony, Peru, the United States, Australasia, South Africa, and in other localities. It occurs either massive or as an alluvial deposit (*stream tin*), and crystallises in tetragonal prisms, terminated by pyramids (Fig. 417). It is a dense mineral (sp. gr. 6·4–7·1), easily separated from lighter rocks by washing. If necessary the ore is crushed, and washed in a current of water, the process being known as *buddling*. If *wolfram* ($FeWO_4$) occurs with the tinstone, it cannot be separated in this way, since its density is 7·1–7·9; recourse is then had to electromagnetic separation (p. 10). The total production of tin in 1913 was 120,300 tons.

Metallurgy of tin.—The ore, after "dressing," *i.e.*, separation from gangue, wolfram, etc., is first *calcined* in an inclined revolving tube-furnace (Oxland and Hocking's calciner) (Fig. 324). The ore is fed in at the top, and meets the flame and hot gas from a furnace at the lower end. Sulphur and arsenic are expelled as sulphur dioxide and arsenic trioxide (As_2O_3), the latter being condensed in flues. Copper and iron form oxides and sulphates. The calcined ore is discharged from the lower end of the furnace; it is cooled and *washed* with water to remove copper sulphate, which goes into solution, and ferric oxide and light matter, which are washed away. The treated ore, known as *black tin*, now contains 60–70 per cent. of SnO_2. It is mixed with one-fifth of its weight of ground anthracite and a little fluor-spar, moistened, and *smelted* in a reverberatory or a shaft furnace: $SnO_2 + 2C = Sn + 2CO$.

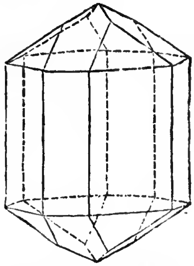


FIG. 417.—Crystal of Tinstone.

The product is **refined** by liquation, *i.e.*, by heating bars of the metal on the hearth of a reverberatory furnace, when the readily fusible tin (m.-pt. 232°) flows away, leaving a dross consisting of an alloy of tin with copper, iron, and arsenic. The metal is finally fused and "poled" with billets of green wood (p. 807), when the remaining impurities separate as a scum. The scum and dross are worked up by smelting. The tin is heated to 200°, when it becomes brittle and can then be broken up by a hammer, yielding *grain-tin*. On slowly cooling molten tin, crystals are formed. The crystalline structure of the metal is destroyed on rolling, *tinfoil* being produced.

Properties.—Metallic tin has a bright white colour, and, after fusion, a specific gravity of 7·30. The metal is very fusible, but has a high boiling point (2270°). Its lustre is not impaired by exposure to air or water, either separately or conjointly, whereas lead is attacked. For this reason tin is used for *tinning* copper or iron vessels. These are first of all thoroughly cleaned, heated, and then molten tin is poured in. This is brushed over the surface of the other metal, rosin and salammoniac being added as fluxes. **Tinplate** is made by dipping clean sheets of iron (given a bright surface by "pickling" in sulphuric acid) into molten tin, covered with melted palm oil. The sheet then passes under a partition in molten tin covered with melted fat, and then through rollers to remove superfluous metal.

Tin is recovered from scrap tinplate by the **detinning process.** The material is washed with alkali to remove grease, rinsed and dried, and heated to melt off the solder. The metal is then treated with chlorine gas in iron cylinders, kept cool. Volatile **stannic chloride**, $SnCl_4$, is formed, and the residue of iron scrap, containing less than 0·1 per cent. of tin, is hydraulically pressed into blocks and smelted in the open-hearth furnace (p. 981).

When ordinary **white tin** is strongly cooled, it crumbles down to a grey powder, of density 5·8. The transformation is quickest at $-50°$. **Grey tin** is an enantiotropic form, the transition point, $Sn\alpha \rightleftharpoons Sn\beta$, being 18°. White tin is thus a metastable form under ordinary conditions; transformation occurs in contact with a little grey tin, or a solution of stannous chloride. Granulated tin, added to the latter, falls to a grey powder. White tin exists in two allotropic forms. From 18° to 170° ordinary tin is stable, and crystallises in the tetragonal system. At 170° transition into a rhombic form, sp. gr. 6·5, occurs :

$$\underset{\text{sp. gr. } 5{\cdot}80}{\text{Grey tin}} \overset{18^\circ}{\rightleftharpoons} \underset{\text{sp. gr. } 7{\cdot}286}{\text{Tetragonal tin}} \overset{170^\circ}{\rightleftharpoons} \underset{\text{sp. gr. } 6{\cdot}56}{\text{Rhombic tin}}$$

Tin oxidises when fused in the air, a grey scum or dross forming on the surface. This consists of a mixture of tin dioxide and unchanged tin : on heating in air it is converted into **tin dioxide,** SnO_2, which is yellow when hot, but becomes white on cooling ("putty powder"). At a white heat tin burns in air with a white flame.

Tin is only slowly attacked by dilute acids, but readily dissolves in hot concentrated hydrochloric acid, forming a solution of **stannous chloride:** $Sn + 2HCl = SnCl_2 + H_2$.

Dilute sulphuric acid slowly forms **stannous sulphate,** $SnSO_4$, with evolution of hydrogen : hot concentrated sulphuric acid gives the same salt and SO_2.

Concentrated nitric acid, when perfectly free from water, has no action, but in presence of a trace of water it acts violently on tin, producing red fumes, and forming a small quantity of soluble tin salt, and an abundant white residue of **metastannic acid,** $H_2Sn_5O_{11}$ (?). Boyle (1670) remarked that "*aqua fortis* eats up more tin than it dissolves." Hot alkalies dissolve tin with evolution of hydrogen, forming stannates.

Tin forms important **alloys,** *e.g.*, *bronze* (p. 810). A mixture of 1 part of tin and 2 parts of lead is ordinary *soft-solder* (*fine-solder* consists of equal parts of tin and lead). *Pewter* contains 4 parts of tin and 1 part of lead, usually with a little antimony. *Britannia metal*, a white metal, consists of 84 tin, 10 antimony, 4 copper, and 2 bismuth. *Mirrors* are sheets of very clean glass backed by pressing them on a surface of amalgamated tinfoil. Tin forms with copper the definite compounds Cu_3Sn and Cu_4Sn. *Phosphor tin* is a white, metallic, coarsely crystalline mass, formed by adding phosphorus to molten tin ; it melts at 370°. The definite compound SnP is known. By adding phosphor tin to molten copper, *phosphor-bronze* is produced (p. 810).

Tin forms **two series of compounds :** the **stannous compounds,** $\overset{II}{Sn}X_2$, and the **stannic compounds,** $\overset{IV}{Sn}X_4$. These correspond with the **oxides,** SnO and SnO_2. The stannous compounds readily pass, by oxidation, into compounds of quadrivalent tin.

Stannous compounds are therefore **reducing agents.** A solution of stannous chloride when added to a solution of mercuric chloride gives first a white precipitate of calomel, and if added in excess a grey precipitate of metallic mercury :

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$$
$$SnCl_2 + 2HgCl = SnCl_4 + 2Hg.$$

If stannous chloride is added to a solution of ferric chloride and potassium ferricyanide, an immediate precipitation of Prussian blue occurs, owing to the reduction of the ferric salt to a ferrous salt : $2Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} = 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}$

The lower oxide, **stannous oxide,** SnO, is *basic*, but the **dioxide,** SnO_2, shows feebly *acidic* properties, forming salts called **stannates,** which are largely hydrolysed in solution : $Na_2SnO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2SnO_3$ (stannic acid). In solution, the stannous salts ionise, with formation of $Sn^{\cdot\cdot}$; stannic salts usually form complex ions, so that the existence of $Sn^{\cdot\cdot\cdot\cdot}$ is doubtful.

Stannous compounds.—Tin (*e.g.*, tinfoil or granulated tin) readily dissolves in hot concentrated hydrochloric acid, a solution of **stannous chloride** being produced : $Sn + 2HCl = SnCl_2 + H_2$. On evaporating and cooling, the solution deposits transparent monoclinic prisms of $SnCl_2,2H_2O$, which melt at 40°. They lose acid on heating, and the anhydrous salt is best prepared by passing hydrogen chloride over heated tin. It is soluble in alcohol and ether, melts at 250°, and boils at 606°, the vapour being associated : $Sn_2Cl_4 \rightleftharpoons 2SnCl_2$. In solution in urethane, the substance has the formula $SnCl_2$. The crystals of hydrated chloride, known as *tin salt*, do not give a clear solution unless hydrochloric acid is added ; with water alone white **stannous oxychloride,** Sn(OH)Cl, is deposited.

Unless granulated tin is added, the acid solution quickly becomes turbid from oxidation, stannous oxychloride being deposited, and stannic chloride remaining in solution: $6SnCl_2 + 2H_2O + O_2 = 2SnCl_4 + 4Sn(OH)Cl$. With concentrated hydrochloric acid, crystalline **hydrochlorostannous acids,** $HSnCl_3$ and H_2SnCl_4, are formed. These form stable crystalline salts, *e.g.*, $(NH_4)_2SnCl_4$. Several compounds of $SnCl_2$ with ammonia are known.

If a piece of zinc is suspended in a solution of stannous chloride, a bright crystalline deposit of tin is formed ("tin tree"). Large crystals of tin are produced by adding zinc dust suspended in water to a solution of stannous chloride.

Stannous bromide, $SnBr_2$, is a light yellow salt, similar to the chloride. **Stannous iodide,** SnI_2, is a red crystalline substance, sparingly soluble in water, but dissolving in hydriodic acid, or iodides, to form **hydriodostannous acid**, $HSnI_3$, or its salts, respectively.

Stannous sulphide, SnS, is formed as a brown precipitate when hydrogen sulphide is passed through an acidified solution of stannous chloride, or as a grey crystalline mass on heating tin with sulphur. The brown precipitate is soluble in hot concentrated hydrochloric acid (arsenic trisulphide is insoluble, *cf.* p. 655); it is not dissolved by alkali-sulphides if these are perfectly free from excess of sulphur, but dissolves readily in the polysulphides, *e.g.*, yellow ammonium sulphide. It then forms first of all yellow **stannic sulphide,** SnS_2, which dissolves in the sulphide to produce a **thiostannate,** *e.g.*, $(NH_4)_2SnS_3$, from which acids re-precipitate stannic sulphide: $(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + H_2S + SnS_2$. The salt $Na_2SnS_3,2H_2O$ is formed by boiling tin and sulphur with caustic soda solution.

Tin dissolves slowly in dilute sulphuric acid, forming **stannous sulphate,** $SnSO_4$; a mixture of 1 vol. of H_2SO_4, 2 vols. of HNO_3, and 3 vols. of water may be used as a solvent. It dissolves in nitric acid diluted with $1\frac{1}{2}$-2 vols. of water, forming **stannous nitrate** and ammonium nitrate: $4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$. On strong cooling, the solution deposits $Sn(NO_3)_2,20H_2O$.

If caustic potash is added to a solution of stannous chloride, a white precipitate of **hydrated stannous oxide,** $2SnO,H_2O$, is produced. On heating at 80°, this loses water and forms **stannous oxide,** an olive-green powder also formed by heating stannous oxalate. This smoulders when heated in air, forming the dioxide, SnO_2. The precipitate of hydrated oxide is soluble in excess of alkali, forming a solution which appears to contain a **stannite,** $H{\cdot}SnO{\cdot}ONa$, analogous to sodium formate: $CO + NaOH = H{\cdot}CO{\cdot}ONa$. The solution has strong reducing properties; *e.g.*, it reduces a solution of cupric sulphate to copper suboxide, Cu_4O.

Stannic compounds.—When tin is treated with excess of chlorine gas in a retort a volatile, strongly fuming, colourless liquid is produced. This is **stannic chloride,** $SnCl_4$, which was discovered by Libavius in 1605, and was called *spiritus fumans Libavii.* He obtained it by distilling tin with corrosive sublimate: $Sn + 2HgCl_2 = 2Hg + SnCl_4$. The vapour-density of stannic chloride (b.-pt. 114·1°) corresponds with the formula $SnCl_4$. With a small quantity of water it dissolves with evolution of heat, forming a clear solution from which the crystalline hydrates, $SnCl_4,3H_2O$, $SnCl_4,5H_2O$ and $SnCl_4,8H_2O$, are obtained. The liquid also contains unchanged $SnCl_4$, which is volatile in steam. The hydrate $SnCl_4,5H_2O$ is prepared in commerce, and is called "oxymuriate of tin," or "butter of tin." Stannic chloride is obtained in detinning scrap tinplate (p. 914). The hydrate is used as a mordant, especially for silk, and in "weighting" the latter. By treating $SnCl_4,5H_2O$ with hydrochloric acid gas at 28°, and cooling to 0°, crystals of **hydrochlorostannic acid,** $H_2SnCl_6,6H_2O$, are formed, melting at 28°. Direct combination of stannic chloride with alkali-chlorides gives **chlorostannates,** *e.g.*, $(NH_4)_2SnCl_6$, which crystallises anhydrous, and was formerly used as a mordant in dyeing madder-reds and pinks (hence it was called "pink salt"), until superseded by $SnCl_4,5H_2O$. The compound $SnCl_4,4NH_3$ is formed directly; it can be sublimed and dissolved in water without decomposition. The compounds $SnCl_4,2SCl_4$, $SnCl_4,N_2O_3$, $SnCl_4,2NOCl$, $SnCl_4,PCl_5$, and $SnCl_4,POCl_3$ all readily formed directly.

Stannic bromide and **iodide** are formed directly. The **fluoride,** SnF_4, is formed from $SnCl_4$ and anhydrous HF.

	$SnCl_4$.	**$SnBr_4$.**	**SnI_4.**	**SnF_4.**
M.-pt.	− 33°	33°	146°	sublimes
B.-pt.	114·1°	201°	295°	705°
Density	2·234(15°)	3·349(35°)	4·696	4·78
	Colourless, strongly fuming liquid.	White, fuming, crystalline solid	Red, stable, octahedral crystals.	White, deliquescent crystals.

The fluoride forms complex salts, *e.g.*, K_2SnF_6, analogous to silicofluorides.

Solutions of halogen compounds of quadrivalent tin contain the un-ionised substances and their hydrolysis products, *e.g.*, **colloidal stannic hydroxide,** $Sn(OH)_4$; the solution in hydrochloric acid contains the ion $SnCl_6''$; and it is doubtful if the stannic ion, $Sn^{\cdot\cdot\cdot\cdot}$, is ever present as such, although $Sn(OH)_4$ dissolves in sulphuric acid, hydroxyl probably being eliminated in stages; $Sn(OH)_4 \rightarrow Sn(OH)_3^{\cdot} \rightarrow Sn(OH)_2^{\cdot\cdot} \rightarrow Sn(OH)^{\cdot\cdot\cdot} \rightarrow Sn^{\cdot\cdot\cdot\cdot}$. From dilute solutions of stannic salts the hydroxide separates as a gelatinous precipitate, especially on boiling: $SnCl_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4HCl$. If the gelatinous form is digested with a solution of potassium sulphate, it becomes granular, filters readily, can be washed, and on ignition forms the **dioxide,** SnO_2.

Stannous compounds are oxidised and can be estimated by titration with standard iodine: $SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI$, or ferric chloride: $Sn^{\cdot\cdot} + 2Fe^{\cdot\cdot\cdot} = Sn^{\cdot\cdot\cdot\cdot} + 2Fe^{\cdot\cdot}$ (p. 255). Stannic compounds are usually estimated by precipitation of the sulphide, SnS_2, which is ignited, and the stannic oxide weighed.

Stannic acids.—The existence of at least two varieties of stannic acid was the first case of isomerism recorded (Berzelius, 1817). **Colloidal stannic acid,** formed in solutions of stannic chloride in water, readily gelatinises. The precipitate is soluble in excess of caustic potash or soda, a solution of a **stannate**, largely hydrolysed and therefore alkaline, being formed: $Sn(OH)_4 + 2NaOH \rightleftharpoons Na_2SnO_3 + 3H_2O$. From the solution, by evaporation, crystals of **sodium stannate,** $Na_2SnO_3,3H_2O$, are obtained. Acids throw down from this gelatinous **α-stannic acid,** which on drying at 100° has the composition H_2SnO_3, and is soluble in dilute acids or alkalies. The solution in dilute hydrochloric acid is identical with a solution of stannic chloride in water. On standing, this solution slowly deposits **β-stannic acid** (*q.v.*), which is probably a polymer of the α-acid.

Sodium stannate, $Na_2SnO_3,3H_2O$, used as a mordant, is prepared by fusing tin dioxide with caustic soda, extracting with hot water, and crystallising. The ignited dioxide, or the mineral tin-stone, is insoluble in all acids except hydrofluoric, and does not dissolve in aqueous alkalies. It can be brought into solution only by fusion with caustic alkalies or their carbonates.

If tin is treated with fairly concentrated nitric acid, stannous nitrate, $Sn(NO_3)_2$, appears first to be formed. This is at once oxidised by the nitric acid to **stannic nitrate,** $Sn(NO_3)_4$, which can be quickly separated if 70 per cent. acid is employed, but usually undergoes hydrolysis. The final product is a white, curdy powder, which is a stannic hydroxide, but differs from α-stannic acid in being insoluble in dilute acids. It is slightly soluble in water, and the solution reddens litmus. This variety of stannic hydroxide is called **β-stannic acid,** or **metastannic acid.** It was formerly supposed to have the formula $H_2Sn_5O_{11}$, but the proportion of water is variable, and the difference between the α- and β-acids seems to be due to something more than varying hydration. If β-stannic acid is warmed with concentrated hydrochloric acid, it is converted into a gelatinous solid hydrochloride, which, on pouring off the hydrochloric acid and adding water, dissolves. β-stannic acid is quickly deposited from the solution, especially on boiling, or on adding sulphuric acid. Cold solutions of alkalies dissolve β-stannic acid, forming **metastannates** (*e.g.*, $Na_2Sn_5O_{11},4H_2O$, a sparingly soluble crystalline powder), from solutions of which acids reprecipitate β-stannic acid. But if β-stannic acid is *fused* with alkali, an α-stannate, from which acids throw down α-stannic acid, is produced.

Colloidal α-stannic acid is formed by dialysing a mixture of stannic chloride solution and potash, or sodium stannate and hydrochloric acid. As the electrolytes pass out, the gelatinous mass first produced gradually forms a clear solution in the dialyser. On heating, β-stannic acid is precipitated.

If β-stannic acid is treated with concentrated hydrochloric acid, a gelatinous mass is produced, which is partly soluble in water. Hydrochloric acid added to the filtrate throws down a white precipitate, which on drying in a vacuum has the composition $Sn_5O_9Cl_2,4H_2O$. It is a glassy mass, soluble in dilute hydrochloric acid, but reprecipitated by the strong acid. It is called **β-stannyl chloride,** but may be a salt of β-stannic acid, which behaves as a weak base. The white powder obtained by the action of concentrated nitric acid on tin may be the corresponding nitrate.

If β-stannic acid is heated with water at 100°, it passes into another form, called **para-stannic acid,** $H_2Sn_5O_{11},2H_2O$ (instead of $H_2Sn_5O_{11},4H_2O$, which is supposed to be β-stannic acid). The identity of these compounds is, however, very ill-defined. Metastannic acid absorbs phosphoric acid almost quantitatively from solutions, and may be used in the separation of this acid in qualitative analysis.

Perstannic acid corresponds with the unknown **peroxide,** SnO_3. By grinding SnO_2 with H_2O_2, and drying the residue at 70°, the compound $HSnO_4,2H_2O$ is obtained; if dried at 100°, $H_2Sn_2O_7,3H_2O$ is formed. By treating a stannate in the same way, **perstannates,** *e.g.*, $KSnO_4,2H_2O$, are formed.

Stannic sulphide, SnS_2.—This compound is formed as previously described (p. 916), or by precipitating a solution of a stannic salt with H_2S. It unites with alkali-sulphides to form **thiostannates** (*loc. cit.*). The precipitate with H_2S is yellow, but becomes black on drying; it is a mixture of the dioxide and disulphide. By adding an acid to a solution of a thiostannate, free **thiostannic acid,** H_2SnS_3, is precipitated, which on heating is converted into golden-yellow SnS_2. Crystalline SnS_2 is obtained as a residue of golden-yellow glistening scales (sp. gr. 4·425) (*mosaic gold*) by heating a mixture of tin filings, sulphur, and salammoniac. It is, in this form, insoluble in acids or alkalies, but dissolves in *aqua regia*:

$$Sn + 4NH_4Cl = (NH_4)_2SnCl_4 + H_2 + 2NH_3$$
$$2(NH_4)_2SnCl_4 + S_2 = SnS_2 + (NH_4)_2SnCl_6 + 2NH_4Cl.$$

LEAD. SEVERAL VARIETIES (p. 462). ORDINARY, Pb = 205·55.

Lead.—The metal lead, which is easily reduced from its ores, is mentioned in Job xix; it was at first confused with tin, but the difference was recognised by Pliny (*cf.* p. 912). The dull, heavy, metal was associated by the alchemists with the slow-moving planet Saturn, and designated by the symbol of the scythe, ♄.

Lead is widely distributed in the mineral kingdom; traces occur in the native form, but the chief ore is *galena*, the **sulphide** PbS, which is a heavy (sp. gr. 7·5) mineral with a bright lustre, found in many parts of the United Kingdom, especially in the north midlands (*e.g.*, Derbyshire) and south-western (Devonshire) counties; it also occurs in Flintshire, and at Leadhills in Scotland. Galena is found in almost every part of the world. It is generally associated with quartz, calcite, fluorite, and barytes, and usually contains 0·01–0·1 per cent. of silver. The **oxides** PbO and Pb_3O_4 (*plattnerite*) are rare minerals; and the **carbonate** *cerussite* ($PbCO_3$): **chlorophosphate** *pyromorphite* ($3Pb_3,(PO_4)_2,PbCl_2$); **sulphate,** *anglesite* ($PbSO_4$); **sulpho-carbonate** (*leadhillite*) ($3PbCO_3,PbSO_4$); and **basic sulphate,** *lanarkite* ($PbO,PbSO_4$) occur less abundantly than galena.

Metallurgy of lead.—Lead is produced from galena by simple roasting in an oxidising atmosphere; its extraction was carried on in England during the Roman occupation, and smelting in Derbyshire was in active operation in the eighteenth century; these mines which were long abandoned, are at present being worked. The process is carried out largely in **reverberatory furnaces** known as **Flintshire furnaces,** introduced in 1698. The ore is first *roasted* at a moderate temperature, when a portion of the galena is oxidised to oxide and sulphate:

(1) $2PbS + 3O_2 = 2PbO + 2SO_2$.

(2) $PbS + 2O_2 = PbSO_4$.

The temperature is then raised, a little quicklime added, and the **smelting** reaction takes place, the remaining lead sulphide reacting with the two oxidised products:

(3) $PbS + 2PbO = 3Pb + SO_2$.

(4) $PbS + PbSO_4 \rightleftharpoons 2Pb + 2SO_2$ (reversible).

With the exception of about 10 per cent., which passes into the slag, all the lead is obtained in the form of metal. The slag is afterwards worked up by heating with lime and powdered coal, either in a small blast furnace, or on the now nearly obsolete Scotch hearth, a flat hearth with a *tuyere* for providing the blast.

Poorer ores, and an increasing amount of richer ores containing quartz, blende, and pyrites, are now smelted in small **blast furnaces.** The ore is first roasted (together with lime), and mixed with coke, old slag, and a flux (consisting of iron pyrites containing silver and gold, which pass into the lead). The lead oxide is reduced by the coke and carbon monoxide, the sulphide by the iron : $PbS + Fe = FeS + Pb$, the sulphate by the sulphide and carbon, and the silicate by carbon and lime or ferrous oxide.

Lead fume (chiefly PbO), formed during smelting, is collected in flues and bag-filters, or by the electrostatic precipitation process.

The crude lead contains copper, antimony, and bismuth, which render it hard. It is *softened* by melting on the hearth of a reverberatory furnace until the foreign metals are oxidised, and form a scum on the surface, mixed with a little litharge (PbO). Lead is also refined by electrolysis (Betts' process) in a solution of lead silicofluoride, with a little gelatin, when a coherent deposit is formed.

Properties of lead.—Lead, if perfectly pure, has a silver-white lustre, but has usually a bluish-grey colour. It is very soft, dense (sp. gr. 11·35), and fusible (m.-pt. 327°). It is plastic, especially when heated, when it may be " squirted " into wire by forcing it through a die under pressure, or " wiped " in forming pipe-joints in plumbing. Tubing is also formed by squirting. The so-called " compo " tubing contains tin. Octahedral crystals of lead are obtained by fusing the metal and allowing to cool, or by precipitating it from a solution of the acetate or nitrate by zinc (" lead tree "). Monoclinic crystals are formed by electrolysis. **Colloidal lead** is produced by reducing a solution of the chloride with hydrazine in the cold. The metal boils at 1140° in a nearly perfect vacuum, the vapour is monatomic at 1870°.

Lead oxidises rapidly but superficially in moist air, a white film of hydroxide and carbonate being deposited. **Pyrophoric lead,** obtained by heating the tartrate, ignites spontaneously in air (p. 166). The metal is not attacked by pure water (except at the boiling point), or by dry air, but is rapidly corroded by water containing dissolved air ; the first product appears to be hydrated plumbous oxide, $Pb_2O,2H_2O$, which rapidly oxidises, forming a loose deposit of plumbic hydroxide, $Pb(OH)_2$, which is appreciably soluble in water, rendering the latter poisonous.

During the action of water containing dissolved oxygen on lead, hydrogen peroxide is produced : $Pb + 2H_2O + O_2 = Pb(OH)_2 + H_2O_2$ —an example of **autoxidation** (p. 342). (On the solvent action of water on lead, see p. 211.)

The **atomic weight** of ordinary lead, determined by conversion of the chloride into silver chloride, is 205·55 ($H = 1$) ; more than one variety of lead, however, exists (*cf.* pp. 462 and 1033).

Lead dissolves readily in dilute nitric acid, or in hot concentrated sulphuric acid, forming salts of the bivalent ion, $Pb^{\cdot\cdot}$, which is colourless, and resembles the barium ion, $Ba^{\cdot\cdot}$, in many ways. It is a powerful cumulative poison, *i.e.*, small quantities below the poisonous dose accumulate in the system, and ultimately induce chronic poisoning. A characteristic symptom of **lead poisoning,** to which painters, plumbers, and potters using lead glazes are subject, is a blue line on the edges of the gums.

Several **complex ions** are known, and lead may form a constituent of anions. Thus, if an alkali is added to a solution of lead salt, a white precipitate of lead hydroxide is formed. This readily dissolves in excess of alkali, forming a solution of a **plumbite,** K_2PbO_2 or $KHPbO_2$, which gives the anions PbO_2'' and $HPbO_2'$, but is largely hydrolysed and reacts alkaline: $PbO_2'' + H_2O \rightleftharpoons PbO + 2OH'$. Ammonia does not dissolve lead hydroxide.

Lead oxides.—The following **oxides of lead** are known:

(1) Pb_2O—**lead suboxide,** formed as a black powder by heating the precipitated oxalate below 300°: $2PbC_2O_4 = Pb_2O + CO + 3CO_2$. It is decomposed by heat, acids, or alkalies into Pb and PbO. Lead also dissolves in a solution of the acetate, forming a sub-salt: $Pb^{\cdot\cdot} + Pb = 2Pb^{\cdot}$.

(2) PbO—**lead monoxide,** basic, ordinary **litharge,** or **massicot.**

(3) Pb_2O_3—**lead sesquioxide,** obtained by adding sodium hypochlorite to a cold solution of PbO in caustic potash. It is a reddish-yellow amorphous powder, decomposed by dilute acids into PbO (soluble) and PbO_2 (insoluble), hence it is probably a **metaplumbate** of lead: PbO,PbO_2

(4) Pb_3O_4—**red-lead** or **minium,** also decomposed by acids, and probably $2PbO,PbO_2$, lead **orthoplumbate.**

(5) PbO_2—**lead dioxide**; weakly basic and acidic, forming salts, PbX_4, and **plumbates,** *e.g.*, K_2PbO_3 and Ca_2PbO_4.

Lead monoxide, PbO.—This oxide is formed on heating lead in air. The grey dross so produced, which consists of a mixture of lead monoxide and metallic lead, if heated in an iron vessel, turns yellow, forming the monoxide PbO. The resulting yellow powder (which darkens on heating) is called *massicot*; if fused, and powdered, the reddish-yellow crystalline form known as **litharge** is obtained. Litharge, obtained in the refining of silver (p. 819), is largely used in making flint-glass (p. 850), in glazing pottery (p. 902), in preparing lead salts, and in making paints and varnishes. It accelerates catalytically the absorption of oxygen by linseed oil, causing the latter to "dry," or form a solid oxidised compound called *linoxyn.* If litharge is boiled with water and olive-oil, **lead oleate,** which is a sticky adhesive mass used in making lead-plaster, is formed, and glycerin passes into solution. Olive oil is triolein, or an oleic ester of glycerin, and is saponified by the lead hydroxide, traces of which are formed by the solution of the litharge (*cf.* p. 776).

Lead hydroxide, which appears to have the formula $2PbO,H_2O$ or $PbO(O_2H)^2$, is formed as a white precipitate on adding an alkali to a solution of a lead salt. It is slightly soluble in water (as is PbO, which first forms the hydroxide), and the solution turns red litmus blue. It appears to ionise as: $Pb(OH)_2 \rightleftharpoons Pb(O_2H)^{\cdot} + OH'$. It dissolves both in acids and bases, forming lead salts and plumbites, respectively. The hydroxide loses water at 145°, forming the monoxide.

Red-lead, or minium, Pb_3O_4.—This important compound is formed by roasting litharge in air at about 400°, and forms a scarlet crystalline powder. It decomposes at 470°: $2Pb_3O_4 \rightleftharpoons 6PbO + O_2$. Red lead is used as a pigment, and in making flint glass.

Lead dioxide, PbO_2.—When red lead is treated with concentrated nitric acid, it is decomposed into lead nitrate and **lead dioxide** (or **lead peroxide**): $Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O$. On washing out the nitrate with water, chocolate-brown lead dioxide, PbO_2, remains. This oxide is always produced when lead compounds are subjected to the action of powerful oxidising agents in presence of alkalies. Thus, it is formed in an impure state when bleaching-powder, or sodium hypochlorite, is added to lead monoxide in alkaline solution: $PbO + NaOCl = PbO_2 + NaCl$. Lead dioxide is also deposited on the *anode* when an acid solution of a lead salt is electrolysed between platinum electrodes; *pure* PbO_2 is formed, and in this way lead may be separated from metals such as copper, which deposit as such on the cathode. A lead plate used as an anode in dilute sulphuric acid is oxidised by the SO_4'' ion discharged: $PbSO_4 + 2H_2O + SO_4 = PbO_2 + 2H_2SO_4$. To bring about the discharge of the SO_4'' ion, 2 × 96,000 cmb. must pass round the circuit from anode to cathode: $SO_4'' + 2 \times 96{,}000$ cmb. $= SO_4$. If this quantity of electricity passes round the circuit in the opposite direction (from cathode to anode), the reaction is reversed: $PbO_2 + 2H_2SO_4 = PbSO_4 + 2H_2O + SO_4 + 2 \times 96{,}000$ cmb. This is the principle of the **lead accumulator.** A lead plate, pasted with a mixture of red-lead and concentrated sulphuric acid, and another plate of lead, are immersed in dilute sulphuric acid. On passing a current from a dynamo, the lead sulphate at the anode is converted into PbO_2 by the above reaction. This is the operation of *charging* the cell, and involves an expenditure of energy, in order to oppose the E.M.F. of polarisation, about 2 volts. On *discharging*, both plates are covered with lead sulphate. On recharging, the sulphate is converted into the dioxide on the anode, and spongy lead on the cathode.

The reactions in the accumulator are:—

+ *anode*: $PbSO_4 + 2H_2O + SO_4'' - 2 \times 96{,}000 \text{ cmb.} \rightleftharpoons PbO_2 + H_2SO_4$.

− *cathode*: $PbSO_4 \rightleftharpoons Pb + SO_4'' + 2 \times 96{,}000$ cmb.

The upper arrows denote the charging, the lower arrows the discharging, reactions.

It is not electricity or electrical energy which is stored in the cell, but **chemical energy**; the material $PbSO_4$ is converted by the expenditure of electrical energy on the cell (leading to the chemical reactions of charging) into the two materials of a primary cell. In the Daniell cell the energy was spent outside the cell in the reduction of the zinc ore to metallic zinc in the smelting process. But whereas the reaction in the Daniell cell is not conveniently reversed by an electric current, so as to put the cell into its initial active form, that in the accumulator is easily reversed by an electrolytic method, with an expenditure of energy practically the same as that obtained in the action of the cell. The latter, therefore, acts as a **reservoir of energy.**

Lead dioxide is a powerful **oxidising agent.** A mixture of the dioxide and sulphur ignites on trituration, burning with a brilliant flame, and forming fumes of lead sulphate. Lead dioxide becomes red hot when exposed to sulphur dioxide, and lead sulphate is produced: $PbO_2 + SO_2 = PbSO_4$. If a manganous salt (*e.g.*, $MnSO_4$) is boiled with concentrated nitric acid, lead dioxide, and a little dilute sulphuric acid, a pink solution of permanganic acid is formed. This is Volhard's test for manganese: $2MnSO_4 + 5PbO_2 + 3H_2SO_4 = 2HMnO_4 + 5PbSO_4 + 2H_2O$. Chromic hydroxide, in presence of an alkali, is oxidised to a chromate.

Plumbates.—If litharge and quicklime are heated together in air, the mass takes up oxygen, forming **calcium plumbate,** Ca_2PbO_4, or $2CaO,PbO_2$: $4CaO + 2PbO + O_2 = 2Ca_2PbO_4$. This may be obtained in nearly colourless crystals, $Ca_2PbO_4,4H_2O$. Calcium plumbate was the intermediate product in Kassner's oxygen process (p. 169). A similar reaction occurs on adding lead dioxide to 100 gm. of caustic potash and 30 gm. of water fused in a silver dish; from the solution in water containing excess of alkali, crystals of **potassium plumbate,** $K_2PbO_3,3H_2O$, or $K_2Pb(OH)_6$, are deposited by evaporating in a vacuum and adding a crystal of the isomorphous stannate. These two salts are derived from **orthoplumbic acid,** H_4PbO_4 or $Pb(OH)_4$, and **metaplumbic acid,** H_2PbO_3, respectively. The former is not known in the pure state; the latter is deposited as a black powder on the anode on electrolysing a slightly alkaline solution of sodium lead tartrate.

Minium, or **red lead,** may be regarded as lead orthoplumbate, $\overset{II}{Pb_2}\overset{IV}{Pb}O_4$; **lead sesquioxide** as lead metaplumbate, $\overset{II}{Pb}\overset{IV}{Pb}O_3$—the sesquioxide is in fact formed on precipitating a lead salt with a solution of a plumbate. When calcium plumbate is heated to 250° in dry air, a **perplumbate,** $CaPb_2O_6$, is said to be formed.

Halogen compounds of lead.—Two series of halogen compounds, $\overset{II}{Pb}X_2$, and $\overset{IV}{Pb}X_4$, are known. These may be called **plumbous,** and

plumbic, compounds, respectively, although the true plumbous compounds correspond with Pb_2O. **Lead dichloride, plumbous chloride,** or simply "lead chloride," $PbCl_2$, is slowly formed on heating the metal in chlorine. Boiling concentrated hydrochloric acid slowly dissolves lead: $Pb + 2HCl = PbCl_2 + H_2$. Lead dichloride is usually prepared, as a white precipitate, by adding a chloride to a solution of a lead salt: $Pb^{\cdot\cdot} + 2Cl' \rightleftharpoons PbCl_2$ (dissd.) $\rightleftharpoons PbCl_2$ (ppd.)

In solution it appears to ionise in two stages: $PbCl_2 \rightleftharpoons PbCl^{\cdot} + Cl' \rightleftharpoons Pb^{\cdot\cdot} + 2Cl'$. The salt is sparingly soluble (1 per cent.) in cold water, more soluble (3·2 per cent.) in boiling water; on cooling the boiling solution anhydrous needles of $PbCl_2$ separate. Lead chloride melts at 485°, and boils at 956°; the vapour density at 1070° corresponds with $PbCl_2$. It dissolves in concentrated hydrochloric acid, forming **hydrochloroplumbic acid,** $HPbCl_3$, salts of which are known. On boiling litharge with a solution of common salt, partial decomposition occurs, with formation of caustic soda (Scheele, 1773): $5PbO + H_2O + 2NaCl \rightleftharpoons 2NaOH + PbCl_2,4PbO$. The residue may be decomposed by lime-water: $PbCl_2,4PbO + Ca(OH)_2 = 5PbO + CaCl_2 + H_2O$, and the reactions have been used in the manufacture of alkali. On heating the residue from the first reaction, a yellow **lead oxychloride,** $PbCl_2,4PbO$, known as *Turner's yellow* (1787), used as a pigment, is formed. Another oxychloride, called *Naples yellow*, or *Cassel yellow*, is prepared by heating litharge with ammonium chloride.

Lead fluoride, PbF_2, and **lead bromide,** $PbBr_2$, are formed by precipitation. **Lead iodide,** PbI_2, is formed as a yellow powder by precipitation. On boiling, it dissolves, and on cooling golden-yellow spangles of the salt separate. It is soluble in a large excess of potassium iodide, forming a double salt, decomposed on dilution. If starch is added to the solution, it becomes blue on exposure to light, indicating decomposition. **Lead chlorate,** $Pb(ClO_3)_2,H_2O$, is formed from litharge and chloric acid. It evolves oxygen and chlorine on heating.

If lead dioxide is dissolved in cold concentrated hydrochloric acid and chlorine passed in, a dark brown solution is formed (Millon, 1842), containing **hydrochloroplumbic acid,** H_2PbCl_6. On adding ammonium chloride to the solution, a yellow precipitate of **ammonium chloroplumbate,** $(NH_4)_2PbCl_6$, is formed. When this is added to cold concentrated sulphuric acid, the free acid, H_2PbCl_6, which is probably first formed, breaks up at once and a yellow liquid, which is **lead tetrachloride,** or **plumbic chloride,** $PbCl_4$, is deposited (Nilkoljukin, 1885). This has a sp. gr. of 3·18, freezes at − 15°, and readily decomposes on warming, with evolution of chlorine: $PbCl_4 = PbCl_2 + Cl_2$. At 105° it explodes.

An orange-coloured solution of hydrochloroplumbic acid is formed by the electrolysis of concentrated hydrochloric acid with a lead anode.

By electrolysis of concentrated sulphuric acid with lead electrodes, **plumbic sulphate,** $Pb(SO_4)_2$, is formed in yellow crystals. **Lead tetrafluoride** is formed by the action of concentrated sulphuric acid on the salt $3KF,HF,PbF_4$, obtained by fusing PbO_2 with KF, and dissolving in HF. This salt on heating first evolves HF, and then fluorine: $3KF,HF,PbF_4 = 3KF,PbF_4 + HF = 3KF + PbF_2 + F_2 + HF$.

On the addition of a *little* water, $PbCl_4$ forms a crystalline hydrate, but it is readily hydrolysed, giving a brown precipitate of hydrated lead dioxide. The ion $Pb^{\cdot\cdot\cdot\cdot}$, in fact, appears (like $Sn^{\cdot\cdot\cdot\cdot}$) to be very unstable; the insoluble dioxide is usually formed when the ion might be expected.

Lead sulphide, PbS.—Lead burns in sulphur vapour, forming a greyish-black mass of **lead sulphide,** PbS, which occurs as the mineral *galena.* The sulphide is also formed as a black precipitate on passing H_2S into a solution of a lead salt. It dissolves in boiling dilute nitric acid, with separation of sulphur; the concentrated acid converts it into a white mixture of $PbSO_4$ and $Pb(NO_3)_2$. The sulphide melts at 1120°, and at higher temperatures sublimes. If H_2S is passed into a solution of a lead salt containing excess of hydrochloric acid, a yellow or red precipitate is first formed, consisting of $PbS,PbCl_2$. This afterwards forms black PbS (*cf.* HgS, p. 876).

Lead pentasulphide, PbS_5, is formed as an unstable purple precipitate on adding a solution of CaS_5 to a solution of a lead salt at 0°.

Lead nitrate, $Pb(NO_3)_2$.—Lead nitrate is deposited in anhydrous milky-white octahedral crystals, isomorphous with $Ba(NO_3)_2$, from a solution of lead, litharge, or lead carbonate in dilute nitric acid (Libavius, "Alchymia," 1595). Concentrated nitric acid precipitates it from aqueous solutions, and lead is not dissolved by the concentrated acid because a protective coating of nitrate is formed. On heating, lead nitrate evolves nitrogen dioxide (with decrepitation): the reaction if carried out in a sealed tube at 357° is reversible: $2Pb(NO_3)_2 \rightleftharpoons 2PbO + 4NO_2 + O_2$. A **basic nitrate,** $Pb(OH)NO_3$, is formed by boiling a solution of the nitrate with litharge.

Lead sulphate, $PbSO_4$.—This salt is formed by adding sulphuric acid to a soluble lead salt. It is a heavy white powder, difficultly soluble in water (1 in 12,000), and almost insoluble in dilute sulphuric acid (1 in 36,500). It dissolves in a warm solution of ammonium acetate ($BaSO_4$ is insoluble), or in hot concentrated sulphuric acid; on cooling the latter solution (6 per cent. $PbSO_4$), crystals of $PbSO_4,H_2SO_4,H_2O$ are deposited. Lead sulphate occurs in crystals as *anglesite,* usually isomorphous with barytes or celestine, but sometimes found as pseudomorphs of galena, and formed by the oxidation of the latter. On boiling with ammonia, a **basic sulphate,** Pb_2SO_5, or $2PbO,SO_3$, is formed. $PbSO_4,3PbO$ also exists.

Plumbic sulphate, $Pb(SO_4)_2$, may be formed in the accumulator: $PbSO_4 + SO_4 = Pb(SO_4)_2$; it is decomposed by water: $Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4$. It is a greenish-yellow substance produced when sulphuric acid is electrolysed below 30° with a lead anode in a porous pot.

Lead chromate, $PbCrO_4$.—This compound is formed as a yellow precipitate, insoluble in dilute, but soluble in concentrated nitric acid (*cf.* $BaCrO_4$), and is used as a pigment (*chrome yellow*). It is probably the least soluble salt of lead.

Basic chromates, of orange or red colour, are obtained when the normal chromate is treated with boiling dilute alkali. Lead chromate is also precipitated when a lead salt is added to a solution of potassium dichromate, but an equilibrium is set up unless an acetate is added: $K_2Cr_2O_7 + Pb(NO_3)_2 \rightleftharpoons 2KNO_3 + PbCrO_4 + CrO_3$. The acetate removes the chromic acid. $PbCrO_4$ dissolves, forming a yellow liquid, in concentrated caustic soda; a complex anion containing lead is produced: $PbCrO_4 + 4NaOH = Na_2PbO_2 + Na_2CrO_4 + 2H_2O$.

Lead cannot, therefore, be separated completely from acid radicals in the ordinary process used in qualitative analysis, viz., boiling with sodium carbonate, if a chromate is present. If the solution is reduced with H_2S, a chromic salt, and a precipitate of $PbSO_4$ are produced.

Mixtures of lead chromate with lead sulphate or barium sulphate are also used as yellow pigments. In calico-printing, the cloth is mordanted with a lead salt, and then steeped in potassium chromate. Lead chromate is used, instead of cupric oxide, in carrying out organic combustion analyses (p. 691) when halogens are present. The lead halides are non-volatile, whereas cupric chloride, etc., are volatile, and pass over into the potash bulbs.

Lead phosphates, $Pb_3(PO_4)_2$, PbP_2O_7, and $Pb(PO_3)_2$.—These compounds are formed as white precipitates on adding the corresponding sodium salts to a solution of lead nitrate or acetate. The orthophosphate dissolves in boiling phosphoric acid, and crystals of the **acid phosphate**, $PbHPO_4$ separate. The compound $Pb_3(PO_4)_2,Pb_2Cl(PO_4)$ occurs as *pyromorphite*; it is isomorphous with the mineral *mimetite*, $Pb_3(AsO_4)_2,Pb_2Cl(AsO_4)$.

Lead borate, $Pb_2B_6O_{11},4H_2O$, used as a paint drier, is formed as a white precipitate; glassy borates are formed by fusing litharge with B_2O_3. With the proportions $3PbO : 2B_2O_3$ a soft yellow glass is formed; with $4B_2O_3$, a paler and harder glass is obtained, whilst with $6B_2O_3$ a hard colourless glass, of high refractive index, results. **Lead silicates,** $2PbO,SiO_2$, PbO,SiO_2, and probably $3PbO,2SiO_2$, are similarly produced. Mixtures of the borates and silicates form **boro-silicate optical glasses.**

Lead acetate.—An important lead salt is the **acetate,** $Pb(C_2H_3O_2)_2,3H_2O$, known as *sugar of lead* on account of its sweet taste. It is prepared by the solution of lead oxide (PbO) or carbonate in hot dilute acetic acid followed by evaporation and crystallisation. Excess of lead oxide must not be added, otherwise a sparingly soluble basic salt is formed. (This also occurs in the preparation of the nitrate). By boiling litharge with a solution of lead acetate, a solution of a **basic acetate,** called *Goulard's extract,* is formed, which is used as a lotion. Two definite basic acetates are known: $PbAc_2,Pb(OH)_2$ and $PbAc_2,2Pb(OH)_2$. By dissolving lead dioxide in warm acetic anhydride *lead tetra-acetate,* $Pb(C_2H_3O_2)_4$, is formed, and separates in stable white needles.

Lead carbonate, $PbCO_3$.—Solutions of lead salts give a white crystalline precipitate of **lead carbonate,** $PbCO_3$ (sp. gr. 6·43), when a solution of a carbonate is added in the cold. The precipitate is sparingly soluble in water (1 in 50,500), but dissolves readily in a solution of ammonium acetate. A complex anion appears to be formed. The **basic carbonate,** $2PbCO_3,Pb(OH)_2$, is prepared as a white pigment, known as *white lead.* Good white lead is an *amorphous* powder, consisting of globules 0·00001–0·00004 in. diameter; it mixes readily with linseed oil, and has a covering-power surpassed only by lithopone. If improperly made, the substance is crystalline and then has a considerable degree of transparency, its covering-power being correspondingly reduced. White lead is readily blackened by sulphuretted hydrogen in the atmosphere. Its adulteration by the cheaper barium sulphate is detected by the insolubility of the latter in dilute nitric acid. *Venetian white* is a mixture of equal parts of white lead and barium sulphate; in *Dutch white* the proportions are one to three.

The old *Dutch process* (described by the Latin Geber) produces a white lead of excellent quality, but is tedious. Lead plates made into rolls, or grids of cast lead, are placed in earthenware pots, with a perforated shelf at the bottom, and vinegar poured in below the shelf. The pots are loosely closed with lead covers and stacked in rows, covered with planks, interstratified with horse-dung or spent tan-bark, the decomposition of which keeps the pots warm and produces carbon dioxide. Basic lead acetate is probably first produced, and is then decomposed by the carbon dioxide, the acetic acid set free again entering into reaction:

(1) $2Pb + O_2 + 2H_2O = 2Pb(OH)_2$ (in presence of air and moisture).
(2) $Pb(OH)_2 + 2CH_3CO_2H = Pb(CH_3{\cdot}CO_2)_2 + 2H_2O$.
(3) $Pb(CH_3{\cdot}CO_2)_2 + H_2O + CO_2 = PbCO_3 + 2CH_3{\cdot}CO_2H$.
(4) $2PbCO_3 + Pb(OH)_2 = 2PbCO_3,Pb(OH)_2$.

The plates after four or five weeks become encrusted with white lead. This is stripped off, washed, and ground. The moist paste is dried in vacuum ovens or kneaded with linseed oil in pug-mills, when water is displaced, the particles of white lead adhering strongly to the oil.

By boiling litharge with lead acetate solution a basic acetate is formed, which is precipitated by a stream of carbon dioxide. The white lead made by this method (*Thenard's process*) is, however, of inferior quality.

A good product is obtained in the *Dale and Milner process*. Four parts of litharge are ground with 1 part of common salt and 16 parts of water for fourteen hours, and carbon dioxide is passed in until the solution is neutral. The *Bischof process* also gives a good quality of white lead. In this, litharge is reduced by water-gas at 250–300°, when the **suboxide,** Pb_2O, is formed. With water this gives the yellow hydroxide, PbOH, which is converted by a current of carbon dioxide into white lead.

Germanium, Ge = 71·9.—The extremely rare element was discovered by Winckler in 1886 in the mineral *argyrodite*, $GeS_2,4Ag_2S$. The metal is easily reduced, and resembles tin and lead, but is brittle. The **oxides,** GeO, GeO_2, are known. The **tetrachloride,** $GeCl_4$, and **germanium chloroform,** $GeHCl_3$, are stable compounds. **Germanium sulphide,** GeS_2, is white, and a gaseous **hydride,** GeH_4, is obtained in an impure state by adding a germanium salt to zinc and dilute sulphuric acid.

Titanium, Ti = 47·72.—This element was discovered by Gregor in 1798 in *ilmenite*, or *titaniferous iron ore*, which is **ferrous titanate,** $FeTiO_3$. The **dioxide,** TiO_2, occurs in the minerals *rutile, brookite*, and *anatase*, and in many rocks, clays, and iron ores. It is a white powder used in forming a yellow glaze on porcelain, and in tinting artificial teeth. **Metallic titanium** (containing carbon) is obtained by reducing the dioxide with carbon in the electric furnace, or (in the pure state) by heating the dioxide with calcium. An alloy with iron, **ferrotitanium,** is prepared by reducing ilmenite with carbon in the electric furnace, and is used in making special steels. The **tetrachloride,** $TiCl_4$, is a colourless, fuming liquid obtained by heating the oxide with carbon in a current of chlorine; it is partly hydrolysed by water. The solution is reduced by zinc and hydrochloric acid to a deep violet **trichloride,** $TiCl_3$, which is a powerful reducing agent. Hydrogen peroxide gives with titanium salts a bright yellow colour, due to the **trioxide,** TiO_3.

Zirconium, Zr = 89·9.—The mineral *zircon* occurs in alluvial sands in Ceylon and in other localities, and consists of *zirconium silicate*, $ZrSiO_4$. From this **zirconium dioxide,** ZrO_2, or **zirconia,** was obtained by Klaproth in 1789. Zirconia is used as a refractory, and (mixed with rare earths) in forming the filaments of Nernst lamps, which become conducting on heating. The **metal** is obtained by reducing a **fluozirconate**, K_2ZrF_6 (*cf.* K_2SiF_6), with potassium, or in the electric furnace. When alloyed with iron it forms a very tough steel.

Thorium, Th = 230·31.—Thorium occurs in the minerals *thorite* (chiefly thorium silicate), *thorianite* (mainly **thoria**, ThO_2), and *monazite*, a phosphate of cerium and lanthanum containing 4–18 per cent. of thoria. Monazite occurs in the form of alluvial sand in India and Brazil. Thorium compounds are used in the manufacture of Welsbach incandescent gas mantles, which consist of cellulose impregnated with a mixture of thorium and cerium nitrates, which on ignition leaves a mixture of 99 parts of thoria and 1 of ceria. Pure thoria emits a relatively feeble light. A **peroxide**, Th_2O_7, is precipitated by alkaline H_2O_2. Thoria is also added in small amounts to tungsten electric lamp filaments (p. 958): it prevents disintegration of the latter in use.

EXERCISES ON CHAPTER XLIV

1. What are the common ores of lead and tin ? How are the metals obtained from these ores ? By what tests would you distinguish lead from tin ?

2. What oxides of lead are known ? How are they prepared ? Describe briefly the properties of these oxides, with special reference to their acidic or basic character.

3. How are the higher chlorides of lead and tin obtained ? What is the action of acids on these metals ?

4. Describe the manufacture of white lead. What substitutes have been proposed for white lead as a paint, and for what reasons ?

5. By what experiments would you demonstrate that stannous salts are reducing agents ? Give equations.

6. By what reactions is tin separated from arsenic in qualitative analysis ? How are the sulphides of tin obtained ?

7. How are the stannic acids and stannates formed ? Do any corresponding lead compounds exist ?

8. Describe the reactions taking place in the charging and discharging of a lead accumulator.

CHAPTER XLV

THE METALS OF THE NITROGEN GROUP

The metals of the nitrogen group.—The **fifth group** in the periodic table includes, besides nitrogen, phosphorus, and arsenic, a number of metals, all of which (except antimony and bismuth) are rare. The group is divided into two *sub-groups*, as follows :

Even series.

Vanadium, V = 50·6
Niobium, Nb = 92·4
Tantalum, Ta = 180·1

Odd series.

Nitrogen, N = 13·897
Phosphorus, P = 30·79
Arsenic, As = 74·37
Antimony, Sb = 119·2
Bismuth, Bi = 206·4

The element niobium is sometimes called **columbium**, Cb. The members of the two sub-groups resemble one another very closely in chemical properties, but differ in some respects. One important difference, which indicates that the division into odd and even series indicated by the periodic classification is not merely arbitrary, is that the members of the even series do not form **organo-metallic compounds** with hydrocarbon radicals, whilst the elements of the odd series form stable compounds of this character. This difference is found throughout the periodic system : the elements of even series do not form organo-metallic compounds except in Group VIII.

All these elements form **typical acidic oxides**, R_2O_5, the acidic character diminishing with increasing atomic weight. The metals vanadium, niobium, and tantalum, in the even series, combine very readily with oxygen, and their compounds are extremely difficult to reduce. They have high melting- and boiling-points and a metallic appearance. The elements of the odd series, on the contrary, are easily reduced from their compounds, have low melting points, and are readily volatilised. In the odd series the gradual transition from typical **non-metals** to typical **metals** is very clearly exhibited. The element phosphorus is decidedly a non-metal, but antimony and bismuth are typical metals, although they are brittle. Arsenic, which stands on the threshold between the two classes, is sometimes regarded as a metal, sometimes as a non-metal ; it shows properties belonging to both groups of elements. Elements of this kind are sometimes called **metalloids**.

Compounds of the two types RX_3 and RX_5 are formed by all the elements of this group ; in addition, some compounds in which the element is bi- and quadri-valent are known. Thus, nitrogen is bivalent in NO ; vanadium forms a dichloride, VCl_2, and a tetrachloride, VCl_4.

ANTIMONY, Sb = 119·2.

Stibnite.—The very earliest records mention under various names a substance used as a pigment, and for painting the eyebrows and face. This latter practice appears to date from prehistoric times ; it was used in Egypt at least as early as 3000 B.C. The black pigment came from Arabia, and was called *stimmi*, afterwards *stibi.* The substance was native **antimony sulphide,** Sb_2S_3, now known as *stibnite.* In II. Kings ix. 30, we find in the translation of St. Jerome : " Porro Jezebel introitu ejus audito pinxit oculos suos stibio," the last word being a literal translation from the Hebrew for stibnite.

Metallic antimony is very easily reduced from stibnite, and a Chaldean vase of date 3000 B.C. was found by Berthelot to consist of pure metallic antimony. The metal, however, was not specifically referred to by ancient writers, and was probably confused with lead. Constantinus Africanus (*c.* A.D. 1050) refers to stibnite as *antimonium*, and the metal was well known to the alchemists. The preparation of metallic antimony and of a number of its compounds is clearly described by Basil Valentine (or Thœlde, see p. 29) in the " Triumphal Chariot of Antimony," Leipzig, 1604, and antimonial compounds had been extensively used in medicine by Paracelsus. The Arabic name for finely-powdered stibnite, *al kohol*, was applied by Paracelsus to the " quintessence," and thence to spirit of wine—*alcohol.*

Metallic antimony.—In the preparation of **metallic antimony,** stibnite, which occurs abundantly near Oporto, is first *liquated*, *i.e.*, heated so that the readily fusible sulphide of antimony (m.-pt. 540°) flows away from the rocky portion. The sulphide is then reduced by heating with iron and a little salt in plumbago crucibles : $Sb_2S_3 + 3Fe = 2Sb + 3FeS$. The metal (*regulus of antimony*) melts, and collects below the slag. The sulphide may also be carefully roasted in a reverberatory furnace, when, at 350°, **antimony dioxide,** Sb_2O_4, is left. At higher temperatures, the **trioxide,** Sb_2O_3 (or Sb_4O_6), sublimes, the arsenic volatilising first as trioxide : $2Sb_2S_3 + 9O_2 = Sb_4O_6 + 6SO_2$. The antimony oxides are mixed with charcoal and sodium carbonate and heated to redness, when reduction occurs : $Sb_4O_6 + 6C = 4Sb + 6CO$. The regulus is purified by fusing with sodium carbonate and a little nitre. It then crystallises on cooling in beautiful star-shaped forms, mentioned by Basil Valentine. The total production of antimony in

1912 was estimated at 35,000 tons, the greater proportion being supplied by France.

Pure antimony is prepared by fusing the pentoxide, prepared by the hydrolysis of recrystallised chlorantimonic acid (p. 937), with potassium cyanide.

Properties of antimony.—Antimony is a silver-white, lustrous metal, sp. gr. 6·8, which is brittle and easily powdered. From the fused metal, on slow cooling, large obtuse rhombohedral crystals are formed, but after rapid cooling the metal has a granular structure. Antimony melts at 630·5°, and boils at 1440°. The vapour densities at 1572° and 1640° correspond with the molecular weights 310 and 284, respectively. These are intermediate between Sb_3 and Sb_4; the vapour possibly consists of $Sb_4 + Sb$, which would correspond with a density of $\frac{1}{2}(120 + 480) = 300$. The metal is precipitated as a fine black powder when zinc is added to a solution of the trichloride; this powder is used in covering plaster casts to give them the appearance of steel.

Antimony is unchanged in air, and is not acted upon by water or dilute acids. It decomposes steam at a red heat, and is oxidised by concentrated nitric acid, giving oxides of nitrogen and a white powder of **antimonic acid**. Antimony dissolves readily in *aqua regia*, forming a solution of the **pentachloride**, $SbCl_5$.

When heated in air antimony burns, evolving white fumes of the trioxide, Sb_2O_3, and tetroxide, Sb_2O_4. A bead of antimony heated on charcoal before the blowpipe continues to burn when the flame is removed: if dropped on a piece of paper turned up at the edges, the bead breaks up into burning globules, which disperse and leave curious charred tracks on the paper.

Allotropic forms of antimony.—Unstable allotropic forms of antimony are known. **Yellow,** or **α-antimony** is produced by the action of ozonised oxygen on liquid stibine, SbH_3 (*q.v.*) at − 90°. It is amorphous, and is slightly soluble in carbon disulphide. Yellow antimony is very unstable, and passes readily at temperatures above − 90° into **black antimony,** an amorphous black powder, sp. gr. 5·3, which is formed directly from liquid stibine and oxygen at − 40°. Black antimony oxidises spontaneously in air, and on warming forms ordinary rhombohedral, or **β-antimony** with evolution of heat. **Amorphous antimony** was obtained by Gore (1858) by the slow electrolysis of a concentrated solution of the trichloride in hydrochloric acid with a platinum cathode and an antimony anode. The metal deposited on the cathode resembles polished graphite, and has a density of 5·78. When scratched, it falls to powder with a slight explosion, evolving fumes of $SbCl_3$, which it always contains to the extent of 4–12 per cent. At 200°, it explodes violently. Amorphous antimony can be kept under water, but if the latter is heated to 75° the antimony explodes. This form is probably a solid solution of $SbCl_3$ in black antimony.

Alloys of antimony.—Antimony is a constituent of several important **alloys**. A mixture of 15 parts of antimony and 85 of lead is *hard lead*, or *antimonial lead*, used for stopcocks for sulphuric acid. The most important alloys of the metal are those used for printers' type. The early printers used wooden type; *metal type* containing antimony is referred to by Basil Valentine as in common use in 1600.

	Lead.	Antimony.	Tin.	Copper.	Zinc.	Bismuth.
Type metal	60	30	10	—	—	—
Linotype metal ...	83·5	13·5	3	—	—	—
Monotype metal ...	80	15	5	—	—	—
Britannia metal ...	—	10·4	85·7	1·0	—	—
Pewter	—	7·1	89·3	1·8	—	1·8
Anti-friction bearing metal	60	20	20	—	—	—

The definite compound, $SbCu_2$, is a beautiful purple alloy.

Oxides of antimony.—Antimony forms two series of compounds, SbX_3 and SbX_5. In solution these appear to give the ions $Sb^{\cdot\cdot\cdot}$ and $Sb^{\cdot\cdot\cdot\cdot\cdot}$, although hydrolysis occurs to a large extent. Three **oxides** are known:

Antimony trioxide, Sb_2O_3 (or Sb_4O_6).
Antimony tetroxide, Sb_2O_4 (or SbO_2).
Antimony pentoxide, Sb_2O_5.

These are all **acidic oxides**, although the trioxide also shows weakly basic properties. It dissolves in cold concentrated nitric acid, forming **antimony nitrate**, $Sb(NO_3)_3$, in hot concentrated sulphuric acid, forming **antimony sulphate**, $Sb(SO_4)_3$, and readily in dilute hydrochloric acid to form the **trichloride**, $SbCl_3$, or in tartaric acid. All the oxides are easily reduced by hydrogen or carbon.

Antimony trioxide, Sb_2O_3, occurs native as *senarmonite* in cubic crystals, and more rarely in rhombic crystals as *valentinite*. It is obtained as a pale buff-coloured powder by digesting antimony oxychloride, $SbOCl$, with a solution of sodium carbonate, or by passing steam over red-hot antimony. From a hot solution in sodium carbonate both forms are deposited in white crystals. Antimony trioxide becomes yellow on heating, being apparently converted into the rhombic form, but becomes white on cooling. It fuses at a red heat, and volatilises at 1560°, the vapour density corresponding with Sb_4O_6. The trioxide dissolves in alkalies, forming salts, *e.g.*, $NaSbO_2.3H_2O$, derived from a hypothetical **metantimonious acid**, $HSbO_2$. The sodium salt is sparingly soluble in water, and crystallises in glittering octahedra. The potassium salt, $K_2O,3Sb_2O_3$, obtained by fusing Sb_2O_3 with potash, is readily soluble in water. If dilute nitric or sulphuric acid is added to tartar emetic (*q.v.*) the precipitate when dried at 100° has the composition H_3SbO_3, **orthoantimonious acid. Pyroantimonious acid**, $H_4Sb_2O_5$, is obtained as a white precipitate by adding copper sulphate to a solution of antimony trisulphide in caustic potash until a white precipitate begins to form (at first a yellow precipitate is thrown down) and then adding acetic acid. Both acids on heating form the trioxide.

Antimony tetroxide, Sb_2O_4, is obtained as a white powder on heating the trioxide in air at 390–775°. At higher temperatures it decomposes into Sb_2O_3. The pentoxide, Sb_2O_5, also forms the tetroxide on heating. Impure Sb_2O_4 is obtained by roasting stibnite; if the oxidation is incomplete, the fused mass is known as *glass of antimony*. It consists of tetroxide with unchanged stibnite, and is used in colouring glass and porcelain yellow. Antimony tetroxide forms salts when fused with alkalies, known as *hypoantimoniates*. If the fused mass obtained from Sb_2O_4 and KOH is boiled with water and the solution precipitated with hydrochloric acid, the salt $K_2Sb_4O_9$, or $K_2O,2Sb_2O_4$, is obtained.

Antimony pentoxide and antimoniates.—Antimony pentoxide, Sb_2O_5, is obtained as a yellow powder by gently heating the solid produced by the repeated evaporation of antimony with concentrated nitric acid. At 440° it decomposes rapidly into Sb_2O_4, and when prepared as described always contains a little lower oxide.

When antimony is fused with potassium nitrate, and the residue extracted with cold water, a white powder of **potassium metantimoniate**, $KSbO_3$, remains, which is soluble in boiling water. Dilute nitric acid precipitates from the solution a hydrated pentoxide, which on gentle heating forms antimony pentoxide, Sb_2O_5, in a pure state. This reddens moist litmus paper, although it is practically insoluble in water. A hydrated form of Sb_2O_5 is also formed by oxidising the trioxide in presence of water with iodine, chlorine, or potassium dichromate. With bromine, nitric acid, or a mixture of potassium chlorate and hydrochloric acid, the oxidation is incomplete. When antimony pentachloride (*q.v.*) is precipitated with hot water, or the trichloride or one of the lower oxides treated with nitric acid, the residue after washing and heating to 100° corresponds in composition with **pyroantimonic acid**, $H_4Sb_2O_7$. At 200°, this is said to form **metantimonic acid**, $HSbO_3$. **Orthoantimonic acid**, H_3SbO_4, is said to be formed by precipitating potassium antimoniate with dilute nitric acid and drying over sulphuric acid in a desiccator.

Pyroantimonic acid dissolves in caustic potash, forming a gummy liquid which deposits potassium metantimoniate, $KSbO_3$, in crystals up to a certain point, but on further evaporation yields a gummy mass. The solution forms with sodium salts a white, amorphous precipitate, possibly $NaSbO_3$, which rapidly becomes crystalline and then consists of **acid sodium pyroantimoniate,** $Na_2H_2Sb_2O_7,6H_2O$, sparingly soluble in cold water (1 in 350), and almost insoluble in alcohol. This is the least soluble sodium salt, and a solution of potassium metantimoniate (obtained from antimony and nitre as described) may be used as a test for sodium salts. A corresponding **acid potassium pyroantimoniate,** $K_2H_2Sb_2O_7,6H_2O$, is obtained by oxidising potassium antimonite with potassium permanganate. **Ammonium metantimoniate,** NH_4SbO_3, is obtained in crystals from a solution of antimonic acid in warm ammonia.

Halogen compounds of antimony.—Halogen compounds of types SbX_3 and SbX_5 are known. Those of type SbX_3 are known with all the halogens; SbX_5 occurs only as SbF_5 and $SbCl_5$.

SbF_3, white solid.
$SbCl_3$, white soft crystals, m.-pt. 73·2°, b.-pt. 223·5°.
$SbBr_3$, white deliquescent needles, m.-pt. 95°, b.-pt. 275°.
SbI_3, three forms, dark-red and greenish-yellow. M.-pt of stable form 171°.

SbF_5, viscous liquid, b.-pt. 155°.
$SbCl_5$, yellow mobile liquid, b.-pt. 140°.

Antimony trichloride, $SbCl_3$.—This compound was prepared by Basil Valentine by distilling roasted stibnite with corrosive sublimate: Glauber (1648) obtained it by dissolving stibnite in hot concentrated hydrochloric acid: $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$. The dark brown solution is distilled; water first passes over, then hydrochloric acid, and finally antimony trichloride, which solidifies in the receiver as a white, crystalline mass (*butter of antimony*).

Antimony trichloride is decomposed by water, with deposition of white basic chlorides. It forms a clear solution with hydrochloric acid, from which crystals of **chlorantimonious acid,** $2SbCl_3,HCl,2H_2O$, may be obtained. In solution, the compound is probably H_3SbCl_6, stable salts of which, R_3SbCl_6, are formed with metallic chlorides. The vapour density of the trichloride, and the boiling point of its ethereal solution, correspond with $SbCl_3$.

Antimonious oxychloride, is precipitated as a white powder when a solution of the trichloride in hydrochloric acid is poured into water. The composition of the precipitate, known as *powder of Algaroth,* varies with the dilution. Two definite oxychlorides are known:

$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$ (formed with a little water);
$4SbCl_3 + 5H_2O \rightleftharpoons Sb_4O_5Cl_2 + 10HCl$ (with a larger amount of water).

With excess of water, especially on heating, hydrated antimony trioxide is formed.

Antimony pentachloride, $SbCl_5$.—This compound is formed by the action of excess of chlorine on the trichloride, or by treating the latter with *aqua regia*. It is a heavy, yellow, fuming liquid, solidifying on cooling (m.-pt. − 6°). The vapour is slightly dissociated at the boiling point, 140° : $SbCl_5 \rightleftarrows SbCl_3 + Cl_2$, but the compound volatilises unchanged at 79° under 22 mm. pressure; the vapour density corresponds with $SbCl_5$ With ice-cold water, two crystalline hydrates, $SbCl_5,H_2O$ (soluble in chloroform) and $SbCl_5,4H_2O$ (insoluble in chloroform), are formed. With excess of water, antimonic acid is produced. When the pentachloride and pentoxide of antimony are heated in the proportion $3SbCl_5 : Sb_2O_5$ at 140°, two **oxychlorides,** Sb_3OCl_{13} (white, deliquescent crystals, m.-pt. 85°) and $Sb_3O_4Cl_7$ (yellowish-white crystals, m.-pt. 97·5°) are formed. With concentrated hydrochloric acid, a fairly stable crystalline **chlorantimonic acid,** $2HSbCl_6,9H_2O$, is formed. This may also be prepared by passing chlorine through a solution of the trichloride in hydrochloric acid, and then adding excess of concentrated hydrochloric acid.

The brown liquid obtained by the action of chlorine on $SbCl_3$ appears to contain a **tetrachloride,** $SbCl_4$, or H_2SbCl_6; stable salts of dark colour, *e.g.*, Rb_2SbCl_6, are known.

Antimony trifluoride, SbF_3, is obtained by distilling antimony with mercuric fluoride, or by dissolving the trioxide in hydrofluoric acid and evaporating. It is not hydrolysed by water. **Potassium fluorantimonite,** K_2SbF_5, prepared by dissolving Sb_2O_3 in a solution of KF in HF, is used in calico-printing. The **tribromide** and **tri-iodide** are formed from the elements; they are decomposed by water, yielding SbOBr and SbOI. The vapour of SbI_3 is scarlet in colour. **Antimony pentafluoride,** SbF_5, is a colourless, oily liquid, without action on glass when dry, obtained by boiling the pentachloride with anhydrous hydrofluoric acid under a reflux condenser for three days and fractionating. The apparatus must be constructed of platinum.

Sulphides of antimony.—Two sulphides of antimony, Sb_2S_3 and Sb_2S_5, are known. The **trisulphide,** Sb_2S_3, occurs as the grey mineral *stibnite*, sp. gr. 4·652. By precipitating a solution of antimony trichloride in hydrochloric acid with sulphuretted hydrogen, a *red* amorphous precipitate is formed, which if dried at 100° and then heated in carbon dioxide to 200° forms the greyish-black modification. The red form is used as a pigment (*antimony vermilion*), and in vulcanising rubber, the red varieties of which contain it. If the black form is heated at 850° in a stream of nitrogen, and the vapour rapidly cooled, lilac-coloured globules of a third form, sp. gr. 4·278, are formed. The red precipitate is insoluble in dilute acids, but dissolves in hot concentrated hydrochloric acid. If the solution, still containing H_2S, is diluted with water, red Sb_2S_3 is precipitated. **Colloidal Sb_2S_3** is formed as an orange-red liquid by adding a 0·5 per cent. solution of tartar emetic to sulphuretted hydrogen water.

Antimony trisulphide is reduced on heating in hydrogen; the reaction is reversible: $Sb_2S_3 + 3H_2 \rightleftharpoons 2Sb + 3H_2S$. It is used, mixed with nitre and sulphur, in the preparation of *blue-fire* in pyrotechny, and in making matches (p. 626). It dissolves in alkali sulphides, and hot concentrated solutions of alkalies and their carbonates. On dilution, a red mixture of Sb_2O_3 and Sb_2S_3 (*Kermes mineral*) is formed. The solutions, and the substances obtained on fusion of Sb_2S_3 with Na_2S, probably contain **thioantimonites,** R_3SbS_3, $R_4Sb_2S_5$, $RSbS_2$.

Precipitated antimony trisulphide is insoluble in ammonium carbonate, whereas arsenic sulphide is soluble (p. 656). It dissolves in fairly concentrated hydrochloric acid on boiling; arsenic sulphide is insoluble.

Thioantimoniates.—When antimony trisulphide is boiled with caustic soda and sulphur, the filtered and cooled solution deposits pale yellow crystals of **Schlippe's salt,** or **sodium thioantimoniate,** $Na_3SbS_4,9H_2O$. The compounds $K_3SbS_4,9H_2O$, $(NH_4)_3SbS_4$, and $Ba_3(SbS_4)_2,6H_2O$ are also known. A solution of the ammonium salt is obtained on dissolving the trisulphide in yellow ammonium sulphide: $Sb_2S_3 + 3(NH_4)_2S_2 + 2S = 2(NH_4)_3SbS_4$. These salts correspond with an unknown **ortho-thioantimonic acid,** H_3SbS_4, or $Sb_2S_5,3H_2S$; on acidification, the acid is not produced but its thioanhydride (*i.e.*, thio-acid − H_2S), **antimony pentasulphide,** Sb_2S_5, is precipitated:

$$2(NH_4)_3SbS_4 + 6HCl = 6NH_4Cl + Sb_2S_5 + 3H_2S.$$

This forms a dark orange-red precipitate, mentioned by Basil Valentine, and by Glauber (1654). On heating alone, or with water or acids, it decomposes into sulphur and the black trisulphide. Antimony pentasulphide readily dissolves in alkalies, even ammonia, and alkali sulphides, forming thioantimoniates:

$$\begin{aligned} Sb_2S_5 + 3Na_2S &= 2Na_3SbS_4; \\ 4Sb_2S_5 + 24KOH &= 5K_3SbS_4 + 3K_3SbO_4 + 12H_2O. \end{aligned}$$

Antimony hydride, SbH_3. — **Antimony trihydride, antimoniuretted hydrogen,** or **stibine,** SbH_3, is formed mixed with hydrogen, when a solution of an antimony salt is added to zinc and dilute sulphuric acid. The gas evolved burns with a white, luminous flame, producing fumes of the trioxide. A black stain of antimony is deposited on a cold porcelain dish held in the flame: $2SbH_3 \rightleftharpoons 2Sb + 3H_2$. This is also formed, on both sides of the heated spot, on passing the gas through a heated glass tube (As is deposited from AsH_3 only on the side furthest from the generating flask).

To distinguish the product from the similar but brighter arsenic mirror, three spots are formed on the dish, which are treated as follows :

(1) Moisten with a solution of bleaching powder :	(2) Moisten with a concentrated solution of tartaric acid :	(3) Moisten with yellow ammonium sulphide, and evaporate :
As dissolves : $5Ca(OCl)_2 + 6H_2O + As_4 = 5CaCl_2 + 4H_3AsO_4$.	As is insoluble.	As gives a yellow residue of As_2S_3.
Sb is insoluble.	Sb dissolves, forming $(SbO)_2C_4H_4O_6$.	Sb gives an orange residue of Sb_2S_3.

Pure stibine is prepared (Stock and Guttmann, 1904) by the action of hydrochloric acid on an alloy of magnesium with 33 per cent. of antimony : $Mg_3Sb_2 + 6HCl = 3MgCl_2 + 2SbH_3$. The gas is washed with water, dried with calcium chloride, and passed into a tube surrounded with liquid air. White solid stibine is formed, which melts at − 88° to a colourless liquid boiling at − 17°. The gas may be collected over mercury, and is fairly stable when dry. It has an unpleasant odour, and is poisonous. It is attacked by air or oxygen, forming water and antimony, and decomposes into its elements in presence of moisture, or with explosion when heated or sparked. The density is slightly higher than that corresponding with the formula SbH_3.

When hydrogen containing stibine is passed into a solution of silver nitrate, a black precipitate is formed, and the filtrate contains no antimony, whereas if arsenic hydride is present, the filtrate contains the whole of the arsenic (p. 649).

The precipitate first formed is **silver antimonide,** $SbAg_3$, but this is rapidly decomposed by the excess of silver nitrate, forming a black mixture of silver, antimonious acid, and a little antimony. If this is warmed with hydrochloric acid, the filtrate gives with H_2S an orange-red precipitate of Sb_2S_3.

Estimation of antimony.—Antimony is **estimated** by precipitation as sulphide, Sb_2S_3, which is heated in a porcelain boat in a stream of carbon dioxide. The trioxide may be dissolved in tartaric acid, neutralised with sodium carbonate, and titrated with iodine : $Sb_2O_3 + 2H_2O + 2I_2 = 4HI + Sb_2O_5$; or a solution in hydrochloric acid may be titrated with sodium bromate :

$$3SbCl_3 + 6HCl + NaBrO_3 = 3SbCl_5 + 3H_2O + NaBr.$$

Antimony pentoxide may be estimated by the reaction :

$$Sb_2O_5 + 4KI + 10HCl = 2SbCl_3 + 4KCl + 2I_2 + 5H_2O.$$

The **atomic weight** of antimony has been determined by heating tartar emetic in hydrogen chloride and weighing the residual potassium chloride: $Sb = 119{\cdot}2$ $(H = 1)$, or $120{\cdot}2$ $(O = 16)$.

Tartar emetic is an important medicinal preparation, obtained by boiling oxide of antimony with water and cream of tartar (potassium hydrogen tartrate). It contains the radical **antimonyl,** SbO, and is **potassium antimonyl tartrate,** $2K(SbO)C_4H_4O_6,H_2O$. It is also used as a mordant.

BISMUTH. $Bi = 206{\cdot}4$.

Bismuth. — Metallic bismuth was probably known to the ancients, but was confused with tin and lead. Agricola (1546) describes it under the name of *bisemutum*, or *plumbum cinereum*, noting that it was used to soften tin. The name is supposed to have been derived from the German *wismuth* (a meadow), given to it by the old miners on account of its red colour. Pott (1739), and later Bergman, investigated its compounds, some of which had been used by Paracelsus for medicinal purposes. The basic nitrate—" bismuth subnitrate," $Bi(OH)_2NO_3$, discovered by Libavius, is still used medicinally in diarrhœa and cholera. This substance, known as *pearl white*, was introduced by Lemery as a cosmetic, and still finds supporters, although it no doubt acts injuriously on the skin by reason of its slight hydrolysis in contact with perspiration, with production of nitric acid. Lemery remarks that its use is injurious.

Bismuth occurs somewhat sparingly, usually in the *native* condition containing arsenic and tellurium, in Bolivia, Saxony, and Australia. The oxide, Bi_2O_3, also occurs, as *bismuthite*, or *bismuth ochre*, but the sulphide, Bi_2S_3, *bismuthine*, or *bismuth glance*, is rare.

The **metal** is obtained from native bismuth by liquation, the ore being heated in sloping iron tubes, when bismuth, which has a low melting point (271°) flows away. The oxide and sulphide ores, which usually contain cobalt and nickel, are first roasted, when the **trioxide,** Bi_2O_3, is formed. This is heated with charcoal, iron, and a flux, and melted in crucibles or in a reverberatory furnace, when metallic bismuth fuses, and collects below the cobalt and nickel arsenides. The crude bismuth is purified by dissolving in dilute nitric acid, pouring the solution of bismuth nitrate, $Bi(NO_3)_3$, into water, calcining the basic nitrate precipitated, and reducing the oxide as before. Very pure bismuth is obtained by reducing the pure oxide with potassium cyanide. The pure oxide is obtained by heating the nitrate, which has been crystallised from a solution containing a large excess of concentrated nitric acid.

Properties of bismuth.—Bismuth is a white metal, sp. gr. 9·78, with a distinctly reddish tinge; it readily forms large crystals on cooling. These crystals, which are obtuse rhombohedra resembling cubes, are usually covered with a superficial film of oxide, and then exhibit a splendid iridescent play of colours. The metal is brittle, and is easily powdered. Bismuth and its alloys with other metals, which have very low melting points, expand when they solidify, and the alloys are used as stereo-metal in printing, the cast being made just before solidification.

Wood's fusible metal (m.-pt. 71°) contains 4 bismuth + 2 lead + 1 tin + 1 cadmium; **Rose's metal** (m.-pt. 93·75°) contains 2 bismuth + 1 lead + 1 tin, and **Lipowitz' alloy** (m.-pt. 60°) consists of 15 bismuth + 8 lead + 4 tin + 3 cadmium. Alloys of lead, bismuth, and tin, melting slightly above 100°, are used in the construction of automatic sprinklers, which discharge a spray of water over combustible goods in warehouses when the fusible metal plug is melted by the rise in temperature resulting from a fire. Fusible solder, which can be applied under hot water containing a little hydrochloric acid, also contains the same materials. Less fusible alloys are used as safety plugs in boilers.

Bismuth boils at 1400°, and the vapour density between 1600° and 1700° shows that partial dissociation occurs: $Bi_2 \rightleftarrows 2Bi$. This is complete at 2000°. The metal is unchanged in dry air, and is only slowly attacked by water. When fused, however, it is slowly oxidised to Bi_2O_3, and when strongly heated burns with a bluish-white flame, forming brown fumes of Bi_2O_3. It decomposes steam slowly, liberating hydrogen. It is not attacked by dilute acids in the absence of oxygen, with the exception of nitric acid, which dissolves it, forming the **nitrate,** $Bi(NO_3)_3$. It also readily dissolves in *aqua regia,* forming the **trichloride,** $BiCl_3$. Boiling concentrated sulphuric acid converts it into the **sulphate,** $Bi_2(SO_4)_3$, sulphur dioxide being evolved. A **colloidal solution** of the metal is formed by reducing the oxychloride with hypophosphorous acid.

Solutions of bismuth salts contain the **ion,** $Bi^{\cdots}$, but they are partly hydrolysed by water, producing precipitates of **basic salts**; these redissolve when an excess of acid is added, the reaction being reversible (*cf.* PCl_3):

$$BiCl_3 + 2H_2O \rightleftharpoons Bi(OH)_2Cl + 2HCl \rightleftharpoons BiOCl + H_2O + 2HCl.$$

Bismuth nitrate, $Bi(NO_3)_3$.—The most important bismuth salt is the **nitrate,** obtained in triclinic crystals, $Bi(NO_3)_3,5H_2O$, by evaporating a solution of the metal in warm 20 per cent. nitric acid. A solution of bismuth in dilute nitric acid, if poured into a large volume of water, deposits the white **basic nitrate,** or "subnitrate," $Bi(OH)_2NO_3$. If this is repeatedly washed with water, white **bismuthous hydroxide,** $Bi(OH)_3$, is left. The hydroxide is also precipitated by alkalies from the solution of the nitrate; it is insoluble in excess of alkali unless glycerol is added, but is readily soluble in acids. When heated to 100° it forms $BiO(OH)$, and on ignition leaves a yellowish residue of **bismuth trioxide,** Bi_2O_3.

If crystals of bismuth nitrate are triturated with mannitol, the mixture gives a clear solution with water. The pure salt can be obtained in solution only if dilute nitric acid is added.

The compounds $BiO(OH)$, $BiOCl$, and $Bi(OH)_2NO_3$ contain the univalent **bismuthyl radical,** $BiO-$, corresponding with $SbO-$. The basic salts obtained by adding a solution of a bismuth salt to water are readily distinguished from the antimony salts by adding a few crystals of tartaric acid and warming. The antimony salts dissolve, but the bismuth salts are insoluble.

Oxides of bismuth.—The following oxides of bismuth have been described :

Bismuth dioxide, Bi_2O_2 (feebly basic).
Bismuth trioxide, Bi_2O_3 (basic).
Bismuth tetroxide, Bi_2O_4 (acidic).
Bismuth pentoxide, Bi_2O_5 (acidic).

Bismuth trioxide, Bi_2O_3, which is obtained by heating the hydroxide, $BiO(OH)$, or directly by heating bismuth nitrate, is a yellowish-white powder which fuses at 820°. On heating to 704°, the powder changes with evolution of heat into a second form, consisting of greenish-yellow crystals. A third form is obtained in yellow needles by heating the oxide in a porcelain crucible to the melting point. Bismuth trioxide is used in producing an iridescent white glaze on porcelain. When mixed with other oxides and fused on the surface of glass, it is used in making stained glass. Thus, with chromium sesquioxide, a lemon-yellow tint is obtained.

Bismuth dioxide, Bi_2O_2, is formed as a black powder on heating the basic oxalate : $(BiO)_2C_2O_4 = Bi_2O_2 + 2CO_2$. It is precipitated on adding a solution of 1 part of stannous chloride to 1 part of bismuth trioxide suspended in caustic potash solution. The black precipitate is washed with dilute potash solution and dried at 100°. Bismuth dioxide burns when heated in air, forming Bi_2O_3. A precipitate consisting of the black dioxide mixed with white bismuth hydroxide or stannous hydroxide is obtained when a solution of a bismuth salt is added to a solution of stannous chloride in excess of caustic soda solution. The formation of a mixture of black and white precipitates so obtained constitutes the **magpie test** for bismuth or tin.

When bismuth trioxide is oxidised with alkaline potassium ferricyanide solution, a brown powder of **bismuth tetroxide,** Bi_2O_4, is obtained. By passing chlorine into a suspension of bismuth trioxide in nearly boiling caustic potash, a scarlet powder of **bismuth pentoxide,** Bi_2O_5, is formed. Both these resemble lead dioxide in colour, and in being insoluble in nitric acid :

$$Bi_2O_3 + 2K_3FeC_6N_6 + 2KOH = Bi_2O_4 + 2K_4FeC_6N_6 + H_2O.$$
$$Bi_2O_3 + 2Cl_2 + 4KOH = Bi_2O_5 + 4KCl + 2H_2O.$$

The higher oxides are reduced when warmed with concentrated hydrochloric or sulphuric acids :

$$Bi_2O_4 + 8HCl = 2BiCl_3 + 4H_2O + Cl_2$$
$$Bi_2O_5 + 3H_2SO_4 = Bi_2(SO_4)_3 + 3H_2O + O_2.$$

On fusing bismuth trioxide with caustic potash in air, a brown mass of **potassium bismuthate,** $KBiO_3$, is formed. This is hydrolysed by water, and Bi_2O_5 is precipitated. The higher oxides of bismuth therefore show *acidic* properties. Potassium bismuthate is used as an oxidising agent.

Bismuth salts.—The most important salts, the **nitrate,** $Bi(NO_3)_3$, and the **basic nitrate,** $Bi(OH)_2NO_3$, have already been described.

Bismuth sulphate, $Bi_2(SO_4)_3$, is obtained by dissolving the metal in hot concentrated sulphuric acid. It forms a **basic sulphate,** $Bi(OH)_4SO_4$, sparingly soluble, on addition of water. On heating, this forms yellow $(BiO)_2SO_4$, **bismuthyl sulphate.** A double salt, $KBi(SO_4)_2$, is formed with potassium sulphate. If sodium thiosulphate is added to a solution of a bismuth salt a clear solution containing **sodium bismuth thiosulphate,** $Na_3Bi(S_2O_3)_3$, is formed. This does not react with iodine. On adding a potassium salt and alcohol to the solution, a sparingly soluble yellow precipitate of the potassium salt, $2K_3Bi(S_2O_3)_3,H_2O$, is formed, and the reaction may be used for the detection of potassium. The solution of the sodium salt quickly decomposes and deposits a black precipitate of bismuth sulphide, Bi_2S_3.

The **basic carbonate,** $2(BiO)_2CO_3,H_2O$, is prepared by precipitating a solution of the nitrate with ammonium carbonate ; on drying at 100° it loses water. **Bismuth phosphate,** $BiPO_4$, and *pyrophosphate,* $Bi_4(P_2O_7)_3$, are obtained by precipitation. The latter fuses to a glassy **metaphosphate** on heating. Bismuth does not readily combine with arsenic or phosphorus.

Bismuth sulphide, Bi_2S_3, is obtained in crystals by fusing bismuth with sulphur, or as a brownish-black precipitate when sulphuretted hydrogen is passed into a solution of a bismuth salt. The precipitate dissolves in nitric acid, and in boiling concentrated hydrochloric acid, but not in alkalies or yellow ammonium sulphide, since it does not, like the sulphides of arsenic, antimony, and tin, form thio-salts in this way. The latter are produced by dissolving the sulphide in concentrated *sodium* sulphide, or by fusion with sulphides. The salts $KBiS_2$ and $NaBiS_2$ form fine crystals with a metallic lustre, rapidly oxidised in the air. On diluting the solution in sodium sulphide, Bi_2S_3, is reprecipitated. Precipitated Bi_2S_3 dissolves in water to the extent of 0·2 mgm. per litre.

Halogen compounds of bismuth.—**Bismuth trichloride,** $BiCl_3$, is formed as a soft, white, crystalline substance, m.-pt. 227°, b.-pt. 428°, on passing an excess of chlorine over bismuth. Its vapour density corresponds with the formula $BiCl_3$. The trichloride is also formed by dissolving bismuth in *aqua regia*. On cooling, crystals of $BiCl_3,H_2O$ are deposited. The solution in concentrated hydrochloric acid deposits crystals of **chlorobismuthous acid,** H_2BiCl_5; at 0° $2BiCl_3,HCl,3H_2O$ is deposited, stable at the ordinary temperature. Salts of H_2BiCl_5, as well as of $HBiCl_4$ and HBi_2Cl_7, have been prepared.

A solution of bismuth chloride when poured into water gives a white precipitate of **bismuth oxychloride,** or **bismuthyl chloride,** $BiOCl$. This is deposited when any bismuth salt is added to a solution of sodium chloride; it resembles silver chloride in becoming grey on exposure to light.

On heating $BiCl_3$ with excess of bismuth, or by heating bismuth with calomel at 250°, a black **dichloride**, $BiCl_2$, corresponding with Bi_2O_2, is formed. It is decomposed by water:

$$3BiCl_2 + 2H_2O = 2BiOCl + Bi + 4HCl.$$

The **tribromide,** $BiBr_3$, is formed from the elements in golden-yellow crystals, decomposed by water into white $BiOBr$. **Bismuth tri-iodide,** BiI_3, is a black powder obtained by adding bismuth oxide to a solution of iodine in stannous chloride saturated with HCl. It is slowly decomposed by water, forming red $BiOI$. Bismuth iodide dissolves in hydriodic acid, forming **iodobismuthous acid,** $HBiI_4,4H_2O$, and in alkali iodides, forming red crystalline salts, *e.g.,* $KBiI_4$. **Bismuth fluoride,** BiF_3, is a white powder obtained by evaporating a solution of Bi_2O_3 in HF. With excess of oxide, $BiOF$ is formed.

The **atomic weight** of bismuth, 206·4 ($H = 1$) has been determined by various methods: conversion of Bi into Bi_2O_3, reduction of Bi_2O_3 to Bi, conversion of $BiBr_3$ into AgBr, and the conversion of Bi into $Bi_2(SO_4)_3$.

Bismuth hydride.—By the action of concentrated hydrochloric acid on an alloy of equal parts of bismuth and magnesium, hydrogen is obtained which on passing through a heated tube deposits a brown mirror of bismuth in front of the heated spot, and a fainter one behind, indicating that traces of the gaseous bismuth hydride (? BiH_3) are formed. Thorium C, an isotope of bismuth, when deposited on magnesium, also gives a radioactive gaseous hydride.

The rare metals of Group V.—Vanadium, niobium (or columbium), and **tantalum** form acidic oxides of the general type R_2O_5, and corresponding salts, usually meta-salts, MRO_3; *e.g.,* ammonium metavanadate, NH_4VO_3. Vanadium forms a complete series of oxides, V_2O_5, V_2O_4, V_2O_3, VO, and V_2O, analogous to the oxides of nitrogen. Compounds of these are produced by reducing a solution of V_2O_5 in dilute sulphuric acid with sulphur dioxide (blue, V_2O_4), magnesium (green, V_2O_3), and zinc (lavender, V_2O). The metal is obtained from V_2O_5 and carbon in the electric furnace ; it is added to special steels. The **chlorides,** VCl_4, VCl_3, and VCl_2, and an **oxychloride,** $VOCl_3$ (*cf.* $POCl_3$), are known.

Niobium and **tantalum** are very rare elements : they form double fluorides, K_2TaF_7, and $2KF,NbOF_3,H_2O$. Metallic **tantalum,** obtained by heating the oxide Ta_2O_5 with aluminium in a vacuum electric furnace, is very resistant to acids, and has a high melting point (2850°) : it was formerly used for electric lamp filaments.

EXERCISES ON CHAPTER XLV

1. How are antimony and bismuth obtained ? For what purposes are the elements, and their compounds, used ?
2. Describe the preparation of antimony hydride. How may it be distinguished from arsenic hydride ? What is known of the hydrides of the other elements of this group ?
3. Starting with antimony, how would you prepare : (*a*) the chlorides, (*b*) the oxides, (*c*) the sulphides ? Compare the properties of these compounds with the corresponding compounds of phosphorus and arsenic.
4. Describe the preparation of four typical compounds from metallic bismuth, mentioning their chief properties and uses.
5. Contrast the properties of the oxides of nitrogen, phosphorus, arsenic, antimony, and bismuth, with special reference to their acidic and basic character, and stability.
6. Describe the preparation and properties of the sulphides of antimony and bismuth. What is the action of ammonium and sodium sulphides on them ?
7. How are the chlorides of antimony and bismuth prepared ? What is the action of water on these compounds ?

CHAPTER XLVI

THE METALS OF THE SULPHUR GROUP

The metals of Group VI.—Group VI of the Periodic System comprises eight elements :

Odd series.		Even series.	
Oxygen,	O = 15·87	Chromium,	Cr = 51·6
Sulphur,	S = 31·81	Molybdenum,	Mo = 95·2
Selenium,	Se = 78·6	Tungsten,	W = 182·5
Tellurium,	Te = 126·5	Uranium,	U = 236·3

At first sight no obvious resemblances exist between the elements of the odd and even series. The former are all non-metals ; the latter all metals. If we take sulphur as representative of the odd series, and chromium as typical of the even series, however, a closer examination of their chemical properties reveals many points of similarity. Both form **acidic oxides,** RO_3, the salts of which are isomorphous, and have similar formulæ :

$$\begin{array}{lll} SO_3 & K_2SO_4\ (K_2O,SO_3) & K_2S_2O_7\ (K_2O,2SO_3) \\ CrO_3 & K_2CrO_4\ (K_2O,CrO_3) & K_2Cr_2O_7\ (K_2O,2CrO_3) \end{array}$$

Polysulphates and polychromates also exist, containing more than $2RO_3$ to one molecule of basic oxide.

Both elements form stable **oxychlorides,** RO_2Cl_2, hydrolysed by water, but there is no chloride of chromium corresponding with S_2Cl_2. The stable chloride of chromium is $CrCl_3$, corresponding with $FeCl_3$ and $AlCl_3$, and chromium shows many resemblances to aluminium and iron. The metals chromium and iron are similar, and the hydroxides, $Al(OH)_3$, $Cr(OH)_3$, and $Fe(OH)_3$, are all precipitated in a gelatinous form by adding ammonia to solutions of the salts. Chromium hydroxide, however, appears to have the formula $Cr_2O(OH)_4$. These three metals are classed together in the same group in qualitative analysis. The analogy between iron and chromium is also seen in the formation of ferrates, *e.g.*, K_2FeO_4 (red), and chromates, *e.g.*, K_2CrO_4 (yellow). The compounds CrX_2 are also closely analogous to the ferrous salts, and differ from the corresponding sulphur compounds.

The elements molybdenum and tungsten resemble chromium in their chemical properties: uranium differs somewhat from its companions, since its stable salts are derived from a radical UO_2, **uranyl.** Molybdenum and tungsten form a number of complex acids with phosphoric acid, etc.

CHROMIUM. $Cr = 51·6$.

Chromium.—A red Siberian mineral containing lead was described, under the name of **crocoisite,** by J. G. Lehmann in 1762, but its composition was only elucidated in 1797 by Vauquelin and by Klaproth, who found that it was a lead salt of **chromic acid,** CrO_3, viz., PbO,CrO_3, or $PbCrO_4$. The name **chromium** (Greek *chroma* = colour) was given to the element because it forms a large number of coloured compounds. Metallic chromium was obtained in an impure state by Vauquelin by reducing the sesquioxide Cr_2O_3 with carbon at a white heat.

The commonest ore of chromium is *chromite*, or *chrome-ironstone*, which is **ferrous chromite,** $FeCr_2O_4$, or FeO,Cr_2O_3, a spinel (p. 891). Rarer minerals are **chrome-ochre,** Cr_2O_3, and **chromitite,** Fe_2O_3,Cr_2O_3.

The **chromates** derived from the acidic **trioxide,** CrO_3, are yellow or red; the **chromic salts,** derived from Cr_2O_3, are violet or green; the **chromous salts,** derived from CrO, are usually blue. The colours are more intense in the hydrated salts.

Chromite is imported mainly from Asia Minor, Rhodesia, and New Caledonia. It occurs in masses with a granular fracture, is very refractory, and is made into chrome bricks used for furnace linings, or to separate the silica bricks outside from the magnesia bricks inside the basic hearth steel furnace (p. 981). Chromite is the source of chromium compounds. If reduced with carbon in the electric furnace, **ferrochrome,** iron with 60 per cent. of chromium, is formed, which is used in the manufacture of *chrome-steel*. This contains 60 parts Cr, 36Fe, and 4 molybdenum, and is free from carbon. It is not attacked by acids, and is usually known as "rustless steel." An alloy of chromium, nickel, and iron is used for making armour-plates.

When powdered chromite is heated to bright redness with lime and a little soda in contact with air, **calcium chromate,** $CaCrO_4$, is formed. The residue is treated with hot sodium carbonate solution, and the filtrate, containing **sodium chromate,** Na_2CrO_4, evaporated. Sulphuric acid is then added, when sodium sulphate is precipitated and a deep red solution of **sodium dichromate,** $Na_2Cr_2O_7$, obtained, from which deliquescent crystals of $Na_2Cr_2O_7,2H_2O$ are deposited after evaporation. In an older process, a mixture of chromite, lime, and potassium carbonate was heated: $4FeCr_2O_4 + 8K_2CO_3 + 7O_2 = 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2$. The yellow solution of **potassium chromate,** K_2CrO_4, obtained on addition of water to the mass was treated with sulphuric acid, and **potassium dichromate,** $K_2Cr_2O_7$, obtained readily in bright red crystals: $2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O$. The sodium salt is much cheaper and more soluble, but may be converted into potassium dichromate by treatment with potassium chloride. Chromates may also be obtained by electrolysing alkalies with an anode of ferrochrome and a cathode of porous copper oxide. Chromates and dichromates are used as oxidising agents, as mordants in dyeing, and in preparing insoluble pigments, *e.g.*, lead chromate, $PbCrO_4$.

EXPT. 329.—Fuse a little powdered chromite with sodium peroxide in a nickel crucible. Extract the cooled mass with water. A yellow solution of sodium chromate is obtained. This is converted into a red solution of the dichromate when sulphuric acid is added.

Metallic chromium.—**Chromium** is obtained by reducing chromium sesquioxide with aluminium in the *thermit process* (p. 894): $Cr_2O_3 + 2Al = 2Al_2O_3 + Cr$. The reaction evolves so much heat that the alumina fuses, and on cooling forms crystalline *corubin.* The chromium forms a fused mass below the alumina, and has a purity of 99·5 per cent. Cr. It contains a little iron and silicon.

In Goldschmidt's thermit process (1898) a mixture of the oxide and aluminium powder in a crucible is ignited by a small cartridge of barium peroxide and magnesium powder placed in a depression in the mixture. This is kindled by a small piece of magnesium ribbon.

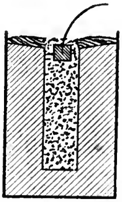


FIG. 418.—Arrangement for Thermit Reaction.

EXPT. 330.—A tin canister, 10 in. by 6 in., is filled with coarsely-powdered fluorspar, and a depression 2 in. × 8 in. made in it by a large test-tube. The mixture of dry chromic oxide and aluminium powder is pressed into this, and the ($BaO_2 + Mg$) igniter placed on the top (Fig. 418). The fluorspar is a good heat insulator, so that a fused mass is obtained even with small amounts of material. A mixture of aluminium powder with an equal, or double, weight of calcium turnings, corresponding with the oxygen of the oxide, acts even more effectively than aluminium alone.

When chromium oxide is reduced by carbon at very high temperatures, the **carbides,** Cr_5C_2 and Cr_3C_2, are formed.

Pure chromium is obtained by electrolysing a solution of chromic chloride, $CrCl_3$, with a mercury cathode, and heating the amalgam in a vacuum to remove mercury.

Chromium is a silver-white, hard, crystalline metal, sp. gr. 6·92, m.-pt. 1615°, b.-pt. 2200°. It burns brilliantly in the oxy-hydrogen flame, forming the sesquioxide, Cr_2O_3. Chromium dissolves in dilute sulphuric and hydrochloric acids, especially on heating, forming blue solutions of **chromous salts**: $Cr + 2HCl = H_2 + CrCl_2$. The blue solutions formed rapidly absorb oxygen on exposure to air, forming green solutions of **chromic salts**: $4CrCl_2 + 4HCl + O_2 = 4CrCl_3 + 2H_2O$. Dilute nitric acid also dissolves chromium, but in the concentrated acid it becomes *passive*, and is then unattacked by dilute acids. Passivity is also induced by exposure to air, or dipping in chromic acid. It is destroyed by touching the metal under the surface of dilute sulphuric acid with zinc. A film of oxide may be the cause of passivity (p. 985). Chromium decomposes steam at a red heat: $2Cr + 3H_2O = Cr_2O_3 + 3H_2$. The finely-divided chromium left on heating the amalgam is pyrophoric; it combines with nitrogen on heating, forming the **nitride** CrN.

Chromous salts.—The **chromous salts**, CrX_2, contain bivalent chromium, and yield the ion $Cr^{\cdot\cdot}$. They are powerful reducing agents. Chromous salts are formed by dissolving the metal in acids, or by reducing chromic salts with zinc and dilute acid: $Cr^{\cdot\cdot\cdot} + H = Cr^{\cdot\cdot} + H^{\cdot}$.

EXPT. 331.—Place 50 gm. of granulated zinc and 50 gm. of finely-powdered potassium dichromate in a flask of 3 litres capacity fitted with a tap-funnel, and a wide delivery tube dipping under water (Fig. 419). Add through the funnel a mixture of 300 c.c. of concentrated hydrochloric acid and 200 c.c. of water. A violent reaction occurs, the liquid first becoming green ($CrCl_3$) and then blue ($CrCl_2$). A saturated solution of sodium acetate is then added (containing 92 gm. of sodium acetate crystals), when a red precipitate of **chromous acetate**, $Cr(CH_3{\cdot}CO_2)_2$, is thrown down. This is fairly stable: it is filtered off, rapidly washed with water saturated with carbon dioxide, and transferred to the flask. The air is expelled from the latter by hydrogen, and the solid dissolved in hydrochloric acid. A blue solution of chromous chloride is formed. This is cooled in ice, and a current of hydrogen chloride gas passed through. **Chromous chloride**, $CrCl_2,4H_2O$, is precipitated in blue needles.

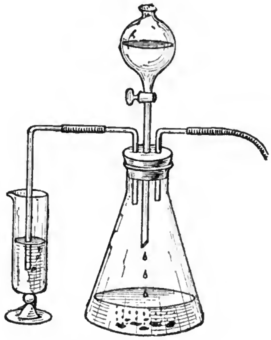


FIG. 419.—Preparation of Chromous Chloride.

Anhydrous chromous chloride is obtained by heating chromic chloride in hydrogen: $2CrCl_3 + H_2 = 2CrCl_2 + 2HCl$, or metallic chromium in hydrogen chloride. It forms *white*, silky needles. The vapour density at 1300° is 113 ($CrCl_2 = 63{\cdot}5$, $Cr_2Cl_4 = 127$); at 1600° it is 89: $Cr_2Cl_4 \rightleftharpoons 2CrCl_2$.

Chromous sulphate, $CrSO_4,7H_2O$, is obtained in fine blue crystals isomorphous with ferrous sulphate by dissolving the acetate in dilute sulphuric acid. It forms double salts, *e.g.*, $K_2SO_4,CrSO_4,6H_2O$.

The ammoniacal solution of $CrSO_4$ absorbs acetylene and nitric oxide.

Caustic soda added to a solution of a chromous salt gives a brownish-yellow precipitate of **chromous hydroxide,** $Cr(OH)_2$, which is readily oxidised in air and in the moist state evolves hydrogen ; in both cases chromic hydroxide is formed : $2Cr(OH)_2 + 2H_2O = 2Cr(OH)_3 + H_2$. **Chromous oxide,** CrO, cannot therefore be obtained by heating the hydroxide ; it is formed as a black powder on exposure of chromium amalgam to air. **Chromous carbonate,** $CrCO_3$, is formed as a yellow precipitate when sodium carbonate solution is added to a solution of chromous chloride.

Chromic oxide, Cr_2O_3.—The **chromic salts** are stable compounds containing tervalent chromium, and correspond with the very stable basic **chromium sesquioxide,** or **chromic oxide,** Cr_2O_3. Chromic oxide is produced as a green powder by heating chromic hydroxide: $2Cr(OH)_3 = Cr_2O_3 + 3H_2O$, ammonium dichromate : $(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$, or potassium dichromate with sulphur: $K_2Cr_2O_7 + S = K_2SO_4 + Cr_2O_3$. A very fine green oxide is produced by gently heating mercurous chromate : $4Hg_2CrO_4 = 8Hg + 2Cr_2O_3 + 5O_2$. The oxide is obtained in dark-green, hard, hexagonal crystals by fusing the amorphous oxide with calcium carbonate and boron trioxide, by igniting a mixture of potassium dichromate and common salt, or by passing the vapour of chromyl chloride, CrO_2Cl_2 (*q.v.*), through a red-hot tube.

The oxide produced by *gentle* ignition of the hydroxide, or of ammonium dichromate, is soluble in acids, and acts as a powerful catalytic agent (*e.g.*, in the oxidation of ammonia, p. 575). The crystalline form, or the *strongly*-ignited oxide, is insoluble in acids, and inactive. It may be brought into solution by fusing with potassium hydrogen sulphate.

Chromic oxide is very refractory (m.-pt. 1990°), but dissolves in fused borax or glass, giving to it a green colour, which becomes blue if strontium is present ; this is applied in tinting glass and painting porcelain. The oxide is also used as a permanent green oil paint under the name of *chrome-green*.

Chromic hydroxide is formed by precipitating a solution of a chromic salt with caustic potash, soda, or ammonia. As ordinarily prepared by precipitating a hot solution with alkali, it is a green, flocculent precipitate, which appears to have the composition $Cr_2O(OH)_4$, *i.e.*, $Cr_2O_3,2H_2O$. By precipitating a cold solution of a violet chromic salt (*q.v.*) with ammonia, a pale blue precipitate, which yields $Cr(OH)_3,2H_2O$ when dried over sulphuric acid, is formed. When heated in hydrogen at 200°, this gives CrO(OH) ; at a red heat this passes into insoluble Cr_2O_3 with incandescence. The blue hydroxide dissolves in caustic soda, giving a grass-green solution which may contain a soluble **chromite,** $Na_2Cr_2O_4$, or Na_2O,Cr_2O_3. Natural chrome-ironstone is ferrous chromite, $FeCr_2O_4$. The green solution may, however, be merely a **colloidal solution** of the hydroxide, since all the chromium hydroxide is deposited on boiling. A dark green colloidal solution is obtained by dialysing a solution of the freshly-precipitated hydroxide in chromic chloride solution. It can be boiled, but is coagulated by salts.

By fusing together equimolecular amounts of potassium dichromate and crystallised boric acid and lixiviating with water, a brilliant green powder, used as a pigment under the name of **Guignet's green,** is left. This is usually supposed to be the hydroxide $Cr_2O(OH)_4$, but always contains boric acid ($3Cr_2O_3,B_2O_3,4H_2O$).

Chromic chloride, $CrCl_3$.—Anhydrous **chromic chloride** is obtained as a sublimate of scaly, peach-blossom coloured crystals when chlorine is passed over a mixture of chromium sesquioxide and carbon heated to whiteness: $Cr_2O_3+3C+3Cl_2=2CrCl_3+3CO$. The crystals volatilise at 1065°, giving a density corresponding with $CrCl_3$. They are almost insoluble in cold water, but readily dissolve in presence of a trace of chromous chloride, giving a green solution.

Three crystalline **hydrates,** $CrCl_3,6H_2O$, are known, two *green* and one *violet*. Precipitated chromium hydroxide dissolves in concentrated hydrochloric acid to form a dark green solution of chromic chloride. If this is cooled in ice and saturated with hydrogen chloride, small emerald-green crystals separate. When these are dissolved in their own weight of water, warmed to 80°, and then cooled to 0°, the solution deposits greyish-blue crystals which dissolve in cold water to give a violet solution. If the crystals are not filtered off, and hydrogen chloride in excess is passed into the solution, a second green form is precipitated.

In solution, the greyish-blue form gives three chloride ions, since all the chlorine can be precipitated with silver nitrate. The first green form gives only two chloride ions, and readily loses a molecule of water. The second green form gives only one chloride ion, and readily loses two molecules of water. Werner (p. 1010) represents the constitution of the three forms as follows:

greyish-blue: $[Cr(OH_2)_6]Cl_3$;
first green: $[Cr(OH_2)_5Cl]Cl_2 + H_2O$;
second green: $[Cr(OH_2)_4Cl_2]Cl + 2H_2O$.

The atoms or molecules inside the square brackets are directly combined with the metal atom, and are not ionisable, whereas those outside are ionisable, or readily split off. The number of atoms or molecules associated with the metal atom is always six.

Chromic fluoride, CrF_3, is obtained in needles by passing HF over $CrCl_3$. The hydrated form, $CrF_3,9H_2O$, is precipitated on adding

NH_4F to a solution of $Cr_2(SO_4)_3$. It forms a violet solution with hydrochloric acid. The **bromide,** $CrBr_3$, and two hydrates, $CrBr_3,6H_2O$, are formed similarly to the chloride. The iodide is unknown.

Chromic sulphate, $Cr_2(SO_4)_3$.—This salt is obtained in violet crystals by allowing a mixture of equal parts of concentrated sulphuric acid and chromic hydroxide (dried at 100°) to stand for some weeks in a loosely-stoppered bottle. If its solution is precipitated with a little alcohol, violet octahedra, $Cr_2(SO_4)_3,18H_2O$, are deposited. With excess of alcohol the anhydrous sulphate is thrown down. Chromic sulphate combines with sulphates of the alkali-metals, forming **chrome alums.**

Potassium chromium sulphate, ordinary **chrome alum,** has the formula $K_2SO_4,Cr_2(SO_4)_3,24H_2O$. It is obtained by reducing a solution of potassium dichromate acidified with sulphuric acid, and hence often separates in purple octahedral crystals on the carbon poles of bichromate cells after use. In these cells zinc and carbon plates are immersed in a solution of potassium dichromate in dilute sulphuric acid. The hydrogen liberated on the carbon plates is oxidised by the chromic acid.

EXPT. 332.—Dissolve 20 gm. of potassium dichromate in 100 c.c. of hot water, and after cooling add carefully 37 c.c. of concentrated sulphuric acid. Pass sulphur dioxide through the solution until the red colour, which at first changes to brown and then to olive-green, has become pure dark green :

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

Evaporate the green solution to about one-fourth its volume, set aside in a covered dish for some time, and observe the formation of purple octahedral crystals of chrome alum. Instead of sulphur dioxide, alcohol may be used in the reduction : the alcohol is oxidised to aldehyde, C_2H_4O.

Chrome alum is formed as a by-product in the oxidation of anthracene, $C_{14}H_{10}$, to anthraquinone, $C_{14}H_8O_2$, by sulphuric acid and potassium dichromate. It is used in dyeing and calico-printing, and in tanning.

In **chrome-tanning** the hides are steeped in a solution of chrome alum. Chromic hydroxide is absorbed by the gelatine of the hide, forming a green, insoluble substance. The dry leather may then be treated with melted paraffin wax to render it waterproof (" driped ").

A solution of chrome alum in cold water has a dull bluish-red colour ; on heating to 70° it becomes green. Barium chloride precipitates the sulphate in the violet solution completely, whilst the green solution is not completely precipitated. If the green solution is allowed to stand for some time in the cold, it becomes violet again and barium chloride precipitates all the sulphate.

A green variety of chromic sulphate is formed by heating the violet crystals, $Cr_2(SO_4)_3,18H_2O$, at 90° until they have the composition $Cr_2(SO_4)_3,8H_2O$. The solution is not precipitated either by alkalies or barium chloride. By the action of sulphur dioxide on chromic acid below 0°, Colson has obtained a green salt, $Cr_2(SO_4)_3,6H_2O$, the freshly-prepared solution of which does not react with barium chloride. On standing, the solution is transformed successively into green substances from which barium chloride precipitates one-third and two-thirds of the sulphate, and finally into a violet solution, completely precipitated by barium chloride. Werner represents the four forms as follows:

$$[Cr_2(SO_4)_3(H_2O)_3] + 3H_2O\ ;\ \ [Cr_2(SO_4)_2(H_2O)_4]SO_4 + 2H_2O\ ;$$
$$[Cr_2(SO_4)(H_2O)_5](SO_4)_2 + H_2O\ ;\ \ \text{and}\ \ [Cr_2(H_2O)_6)](SO_4)_3.$$

A number of complex chromic-sulphuric acids and other salts are known.

Chromium nitrate, $Cr(NO_3)_3,9H_2O$ is formed from the hydroxide and nitric acid. The **phosphate,** $CrPO_4$, is formed by precipitation of chromium salts with sodium hydrogen phosphate as an amorphous violet precipitate. On standing for a day or two in contact with the solution this is converted into a violet crystalline hexahydrate, $CrPO_4,6H_2O$. If allowed to stand for a week in the solution, the amorphous precipitate is converted into a green *amorphous* tetrahydrate, $CrPO_4,4H_2O$ A green *crystalline* tetrahydrate is formed by boiling the violet hexahydrate with water for half an hour. On heating, all the hydrates give a black powder of $CrPO_4$. **Chromic acetate** is obtained as a green solution, used as a mordant, by dissolving the hydroxide in acetic acid.

Chromium sulphide, Cr_2S_3, is obtained by heating sulphur with chromium, or $CrCl_3$ in H_2S. By adding a solution of ammonium sulphide to a chromic salt, the hydroxide is precipitated, as the sulphide is completely hydrolysed by water: $2CrCl_3 + 6H_2O + 3(NH_4)_2S = 2Cr(OH)_3 + 6NH_4Cl + 3H_2S$.

Chromium trioxide or chromic acid, CrO_3.—By the action of concentrated sulphuric acid on a solution of a dichromate, red **chromium trioxide,** CrO_3, is obtained. This substance is often called "chromic acid," although this should have the formula H_2CrO_4. True chromic acid is said to be formed by warming the trioxide with a little water and cooling, but if it exists it is very unstable. The aqueous solution of chromium trioxide has a red colour and is strongly acid. The depression of freezing point and the conductivity show that the solution contains **dichromic acid,** $H_2Cr_2O_7$, which is not known in the pure state.

EXPT. 333.—Dissolve 50 gm. of $K_2Cr_2O_7$ in 85 c.c. of water, and to the cooled solution add slowly 70 c.c. of concentrated H_2SO_4. Allow to stand for twelve hours and pour the liquid off the crystals of acid potassium sulphate which have separated: $K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O$. Heat to 85°, add 25 c.c. of sulphuric acid and sufficient water just to dissolve the CrO_3 separating. Allow to stand twelve hours, and decant the liquid from the crystals of CrO_3. Wash the latter in a Büchner funnel containing asbestos with pure nitric acid, and heat to 60–80° in a current of air in a tube to remove the adhering nitric acid.

Chromium trioxide forms a deliquescent red woolly mass or red lustrous rhombic prisms. It melts at 193° to a dark red liquid, solidifying on cooling to a reddish-black mass with a metallic lustre. At 250° it loses oxygen: $4CrO_3 = 2Cr_2O_3 + 3O_2$; a little of the trioxide sublimes. Chromium trioxide is a very **powerful oxidising agent.** Alcohol dropped on it catches fire; the concentrated solution is reduced by sugar, oxalic acid, paper, cork, etc. It oxidises sulphur dioxide, hydrogen sulphide, stannous chloride, arsenious oxide, ferrous salts, etc. In acid solutions the reduction always proceeds to the stage of a chromic salt: $2CrO_3 = Cr_2O_3 + 3O$. A solution of potassium dichromate mixed with sulphuric acid is very often used in organic chemistry as an oxidising agent; a solution of chromium trioxide in glacial acetic acid (which is not oxidised) is also applied.

Chromates.—Chromic acid in its salts shows the closest analogies to sulphuric acid, and its formula may be written $CrO_2(OH)_2$. It forms **normal chromates** (*e.g.*, K_2CrO_4), and **dichromates** (*e.g.*, $K_2Cr_2O_7$), analogous to sulphates and disulphates. Acid chromates, *e.g.*, $KHCrO_4$, are not known, but by the action of excess of CrO_3, or by boiling the dichromate with nitric acid, **trichromates** (*e.g.*, $K_2Cr_3O_{10}$, or $K_2O,3CrO_3$) and **tetrachromates** (*e.g.*, $K_2Cr_4O_{13}$, or $K_2O,4CrO_3$) are formed as red crystals.

Normal potassium chromate, K_2CrO_4, is obtained in lemon-yellow crystals by neutralising a solution of chromic acid or the dichromate with caustic potash or potassium carbonate, and evaporating. It is isomorphous with potassium sulphate. **Potassium dichromate,** $K_2Cr_2O_7$ (p. 947), may be obtained by adding the requisite amount of sulphuric acid to a saturated solution of the normal chromate, and crystallises out on cooling in garnet-red crystals. The solubilities of the two salts are as follows, in 100 parts of water:—

	0°	30°	60°	105·8°	104·8°
K_2CrO_4	54·57	65·13	74·60	88·8 (b.-pt.)	—
$K_2Cr_2O_7$	4·64	18·13	45·44	—	108·2 (b.-pt.)

Both salts are non-deliquescent: they crystallise without water. **Sodium chromate,** $Na_2CrO_4,10H_2O$, and **dichromate,** $Na_2Cr_2O_7,2H_2O$, made on a large scale, are deliquescent. A solution of sodium chromate is produced by triturating moist chromium hydroxide with sodium peroxide. **Ammonium chromate,** $(NH_4)_2CrO_4$, is unstable; it is obtained by crystallising solutions containing excess of ammonia. **Ammonium dichromate,** $(NH_4)_2Cr_2O_7$, is readily obtained by adding ammonia to the requisite amount of chromium trioxide in solution. It forms orange-red crystals which decompose violently on heating, evolving nitrogen and steam and leaving a voluminous dull-green mass of chromic oxide. All soluble chromates are poisonous.

Metallic chromates, if soluble, are formed from the oxides and chromic acid; they are often insoluble and can then be prepared by double decomposition. The most important sparingly soluble chromates are:

Silver chromate: Ag_2CrO_4; brick-red, soluble in acids and ammonia.

Barium chromate: $BaCrO_4$; yellow, insoluble in acetic acid, soluble in mineral acids.

Zinc chromate (basic): $Zn_2(OH)_2CrO_4,H_2O$; yellow.

Lead chromate: $PbCrO_4$ (*chrome-yellow*—used as a pigment)—precipitated from $Pb(NO_3)_2$ and $K_2Cr_2O_7$; soluble in nitric acid and in caustic potash.

Basic lead chromate: Pb_2CrO_5 (*chrome-red*—used as a pigment)—by digesting $PbCrO_4$ with cold caustic soda; mixed with $PbCrO_4$ it forms the pigment *chrome-orange*.

Bismuth chromate (basic): $2(BiO)_2CrO_4,Bi_2O_3$; lemon yellow.

Chromic chromate: $Cr_2O_3,CrO_3 = 3CrO_2$ (**chromium dioxide**)—by heating chromic nitrate, or precipitating a chromic salt with a chromate.

Potassium dichromate in acid solution liberates iodine from potassium iodide: $K_2Cr_2O_7 + 7H_2SO_4 + 6KI = Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$. It is used in volumetric analysis for the estimation of ferrous iron. In acting as an oxidising agent it is reduced to a chromic salt: $K_2O,Cr_2O_6 = K_2O + Cr_2O_3 + 3O$. One gm. molecule therefore contains 3 atoms, or 6 equivalents, of available oxygen; a decinormal solution, containing 0·1 equivalent of available oxygen per litre, is produced by dissolving 4·913 gm. of $K_2Cr_2O_7$ in a litre of water. This oxidises ferrous salts in acid solution according to the equation: $2FeO + O = Fe_2O_3$, hence 1 equivalent of oxygen (10 litres of $N/10K_2Cr_2O_7$) oxidises *two* equivalents of ferrous iron, or 56 gm. The titration of the ferrous salt is complete when a drop of the liquid, brought in contact with a drop of freshly-prepared potassium ferricyanide solution on a white plate, no longer gives a blue colour (p. 248).

Chromyl chloride, CrO_2Cl_2.—Chromium, and the other metals of the chromium group, form **oxychlorides,** containing the bivalent radicals RO_2, *viz.*, RO_2Cl_2:

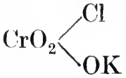
chromyl chloride, CrO_2Cl_2	**tungstyl chloride,** WO_2Cl_2
molybdyl chloride, MoO_2Cl_2	**uranyl chloride,** UO_2Cl_2

When a mixture of sodium chloride and potassium dichromate is distilled in a retort with concentrated sulphuric acid, a deep red vapour is produced, which condenses to a nearly black liquid like bromine. This is **chromyl chloride,** CrO_2Cl_2. If chromium trioxide is dissolved in concentrated hydrochloric acid, and concentrated sulphuric acid added in small quantities at a time to the cooled liquid, chromyl chloride separates, and may then be distilled : $CrO_3 + 2HCl \rightleftharpoons CrO_2Cl_2 + H_2O$. It boils at 115·9°, and is decomposed violently by water, with production of chromic and hydrochloric acids. The vapour density corresponds with the formula CrO_2Cl_2. Chromyl chloride is a powerful oxidising agent, exploding in contact with phosphorus (*cf.* Br_2) and inflaming sulphur, ammonia, alcohol, and many organic substances. Bromides and iodides do not produce corresponding compounds when distilled with dichromate and sulphuric acid, but the free halogen is liberated : this may be utilised in the detection of chlorides in presence of bromides and iodides, since if the former is present the distillate, when collected in water, produces chromic acid, and gives with lead salts a yellow precipitate of $PbCrO_4$.

Chlorochromates.—When powdered potassium dichromate is dissolved in warm concentrated hydrochloric acid, and the liquid cooled, or if chromyl chloride is added to a saturated solution of potassium chloride, red crystals of **potassium chlorochromate,** $KCrO_3Cl$, are formed :

$$K_2Cr_2O_7 + 2HCl = 2KCrO_3Cl + H_2O$$
$$CrO_2Cl_2 + KCl + H_2O = KCrO_3Cl + 2HCl.$$

This salt is known, after its discoverer, as **Peligot's salt** ; it probably has the constitution



$CrO_2\begin{cases} Cl \\ OK \end{cases}$

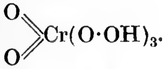
and is the salt of an unknown **chlorochromic acid,** [*cf.* chlorosulphonic acid, $SO_2(OH)Cl$] :

$CrO_2(OH)_2$	$CrO_2(OH)Cl$	CrO_2Cl_2.
(hypothetical) **chromic acid.**	(hypothetical) **chlorochromic acid.**	**chromyl chloride.**

The salt is partly decomposed by water, and decomposes at 100° with evolution of chlorine (*cf.* p. 222) $4CrO_2(OK)Cl = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_2$. When it is suspended in ether and treated with dry ammonia, stable red crystals of the **amino-chromate,** $CrO_2(OK)NH_2$, are formed. If this substance is treated in an ethereal solution of ammonia with chlorine, brown **chromylamine,** $CrO_2(NH_2)_2$, is deposited.

Perchromic acid.—If hydrogen peroxide is added to an aqueous solution of chromic acid, or of a chromate acidified with sulphuric acid, a dark coloured liquid is produced which on agitation with ether gives a deep indigo-blue colour to the latter (p. 340). This blue ethereal solution contains a higher oxygen compound of chromium, called **perchromic acid.** On evaporation, or addition of alkalies, oxygen is evolved, and a chromic salt is formed.

By the action of organic bases (aniline, pyridine, etc.) on the blue ethereal solution, *deep-blue* salts are formed which are explosive. These have been represented as $CrO_4(OR),H_2O_2$, *i.e.*, derived from $HCrO_5$, or as acid salts, RH_2CrO_7, derived from H_3CrO_7. From alkaline chromate solutions and H_2O_2, *red* salts are obtained, of the formula R_3CrO_8, which on treatment with acids evolve oxygen and form the blue salts. **Free perchromic acid** is obtained by adding 97 per cent. H_2O_2 to a solution of CrO_3 in methyl ether cooled to $-30°$, pouring off the blue liquid from excess of CrO_3, and evaporating in a vacuum at $-30°$. The dark blue, crystalline mass decomposes at a temperature slightly above $-30°$. Its composition corresponds with the formula $H_3CrO_8,2H_2O$, but the water may be constitutional and the formula $(OH)_4Cr(O{\cdot}OH)_3$. The red salts may be anhydro-salts of the blue acid, viz.,



$$\begin{matrix}O \\ | \\ O\end{matrix}\!\!>Cr(O{\cdot}OH)_3.$$

Molybdenum, Mo = 95·2.—The mineral *molybdenite* resembles graphite in appearance, but was shown by Scheele (1778) to consist of **molybdenum sulphide,** MoS_2. When roasted in air it leaves a residue of **molybdenum trioxide,** MoO_3 ("molybdic acid"), which dissolves in ammonia to form *ammonium molybdate,* $(NH_4)_2MoO_4$. The crystals obtained by evaporation (ordinary "ammonium molybdate") are more complex, $(NH_4)_6Mo_7O_{24},7H_2O$. Molybdenum and tungsten show marked tendencies to form such **complex compounds.** A solution of ammonium molybdate in nitric acid gives with phosphoric acid a canary-yellow precipitate of **phosphomolybdic acid,** which when dried at 100° has the composition $(NH_4)_3PO_4,12MoO_3$. The **chlorides** $MoCl_5$, $MoCl_4$, $MoCl_3$, and $MoCl_2$ are known, as well as the **hexafluoride,** MoF_6 (*cf.* SF_6). **Molybdenum** is a white metal of high melting point (2450°) obtained by reducing the trioxide with aluminium (*cf.* Cr). Its alloy with iron (**ferromolybdenum**) is prepared by reducing molybdenite with iron and carbon in the electric furnace: steel containing 2 per cent. of molybdenum does not soften on heating and is used for high-speed lathe tools.

Tungsten, W = 182·5.—The heavy mineral now called *scheelite* was found by Scheele in 1781 to be **calcium tungstate,** $CaWO_4$. A commoner mineral is *wolfram,* **ferrous tungstate,** $FeWO_4$, found with tinstone in Cornwall (p. 10). If these minerals are boiled with hydrochloric acid, a yellow powder of **tungsten trioxide,** WO_3 ("tungstic acid"), remains. If this (or wolfram) is fused with sodium carbonate, soluble **sodium tungstate,** a complex salt, $Na_{10}W_{12}O_{41},28H_2O$, is obtained, which is used as a mordant and in rendering flannelette non-inflammable. **Colloidal tungstic acid** is obtained by dialysing a solution of sodium tungstate to which hydrochloric acid has been added. **Phosphotungstic acid,** obtained from sodium tungstate and phosphoric acid, is soluble in ether and is used as a reagent for alkaloids. **Metallic tungsten** is obtained by reducing the trioxide with hydrogen at a red heat: **ferrotungsten,** obtained in the electric furnace, is used for special steels (7–9 per cent. of W; 2–3 per cent. of Cr). Tungsten filaments (m.-pt. 3100°) are used in electric lamps.

The compounds WF_6 (gas), WCl_6, WCl_5, WCl_4, and WCl_2 are known.

Uranium, U = 236·3.—The black mineral *pitchblende,* found in Bohemia, Saxony, East Africa, and Colorado, was found by Klaproth (1789) to be the oxide of a metal which he called **uranium**: U_3O_8. Other uranium minerals, *e.g.*, *carnotite,* a vanadate of uranium and potassium (23 per cent. of U) are found. All these ores contain traces of **radium** (p. 1021). If pitchblende is dissolved in concentrated sulphuric acid, the lead, etc., separated by H_2S, and ammonia added to the filtrate, a precipitate of ferric hydroxide and **uranyl hydroxide,** $UO_2(OH)_2$, is formed, from which ammonium carbonate dissolves the uranium, forming a crystalline compound, $UO_2CO_3,2(NH_4)_2CO_3$, which on ignition yields the pure oxide, U_3O_8. When this is dissolved in nitric acid, yellow, fluorescent crystals of **uranyl nitrate,** $UO_2(NO_3)_2,6H_2O$, commonly called "uranium nitrate," separate. Uranium salts mostly contain the bivalent **uranyl radical,** UO_2. They are used in photography and in making fluorescent glass. The **chlorides** UCl_5, UCl_4, and UCl_3, and the **fluoride,** UF_5, are known. The **oxychloride,** UO_2Cl_2 (*cf.* CrO_2Cl_2), is formed by heating the oxide with charcoal in chlorine. The **metal** is obtained by reducing UCl_4 with sodium. Alloys with iron are obtained in the electric furnace, and used in making special steels.

EXERCISES ON CHAPTER XLVI

1. Discuss the inclusion of chromium in the sulphur group. With what other elements does chromium show analogies?

2. In what forms does chromium occur? How is sodium dichromate manufactured from chromite, and for what purposes is it used?

4. How would you prepare (*a*) chromium trioxide, (*b*) chromyl chloride, (*c*) chromium sesquioxide, (*d*) chrome alum, (*e*) chromous chloride, from potassium dichromate? Describe the properties of these substances.

4. How are chromium, molybdenum, and tungsten obtained? For what purposes are they used?

5. What are the general properties of (*a*) chromous salts, (*b*) chromic salts? In what forms does chromic sulphate exist? What explanation of the existence of these forms has been given?

6. What happens when potassium dichromate is: (*a*) warmed with concentrated hydrochloric acid; (*b*) boiled with concentrated sulphuric

acid ; (*c*) treated, in a solution acidified with sulphuric acid, with sulphur dioxide ; (*d*) treated with zinc and dilute hydrochloric acid ; (*e*) added, in solution, to acidified hydrogen peroxide ?

7. How is perchromic acid obtained ? What is the formula of this substance ?

8. How is ammonium molybdate obtained from molybdenite ? What happens when this salt is added to a solution of a phosphate acidified with nitric acid.

CHAPTER XLVII

MANGANESE. $Mn = 54{\cdot}49$

Manganese.—The position of manganese in the seventh group of the periodic system is one of isolation. The only property in which it shows analogies with the halogen elements is the formation of a higher oxide, Mn_2O_7, which forms salts, **permanganates,** *e.g.*, $KMnO_4$, isomorphous with perchlorates, *e.g.*, $KClO_4$. The oxide Mn_2O_7 is also volatile and explosive like Cl_2O_7. Both silver perchlorate and silver permanganate are sparingly soluble in water.

In its remaining compounds manganese shows much closer analogies with chromium and iron, the two elements of adjoining groups in the same series (see the periodic table). The metals are similar in physical properties, and both manganese and chromium form basic sesquioxides, dioxides, and acidic trioxides. Potassium chromate (yellow), K_2CrO_4, and potassium manganate (green), K_2MnO_4, are isomorphous. The salts corresponding with the sesquioxide, Mn_2O_3, *e.g.*, $Mn_2(SO_4)_3$, are much less stable than those of chromium, *e.g.*, $Cr_2(SO_4)_3$. Manganese resembles iron in forming three oxides of the types RO, R_2O_3, and R_3O_4, the first two of which form series of salts. The manganous salts, however, are more stable than the ferrous salts, *e.g.*, they do not undergo oxidation on exposure to air. Manganese resembles magnesium in forming a sparingly soluble compound, $MnNH_4PO_4$ (p. 859).

Manganese ores.—The most important ore of manganese is the black dioxide, MnO_2, known as *pyrolusite.* This is referred to by Pliny as " magnesia," but was confused with an ore of iron, the magnetic oxide, Fe_3O_4. The name *pyrolusite* (Greek *pyr*, fire; *luo*, I dissolve) refers to the use of the mineral in decolorising glass. The materials used in making glass usually contain iron, and the ferrous silicate produced gives a green colour to the glass. If pyrolusite is added in small quantity, the ferrous silicate is oxidised to ferric silicate, which has a pale yellow colour, neutralised by the purple tinge imparted by the manganese. Pott in 1740 and Scheele in 1774 investigated pyrolusite; metallic manganese was first obtained in an impure form by Gahn, by heating the mineral with carbon: $MnO_2 + 2C = Mn + 2CO$.

Pyrolusite occurs in many localities such as Bohemia, Spain, India, and North America. It is usually contaminated with barium, often in the form of *psilomelane*, $(Mn,Ba)O,2MnO_2$, and with ferric oxide. Pyrolusite always contains less oxygen than corresponds with the formula MnO_2; if used for the manufacture of chlorine by the Weldon process (p. 240), the ore is valued on its content of available oxygen. Most of the ore is now used in smelting for ferromanganese, and the manganese content is of more importance. About 700,000 tons of manganese ores are produced annually.

Less important manganese minerals are the oxides, *braunite*, Mn_3O_3; *hausmannite*, Mn_3O_4; the hydrated sesquioxide, *manganite*, Mn_2O_3,H_2O; hydrated dioxides, *wad* and *psilomelane*; the carbonate, *dialogite*, $MnCO_3$; the silicate, *rhodonite*, $MnSiO_3$; and the sulphide, *alabandite*, MnS. The deposits of hydrated oxides are sedimentary (precipitates, or derived from oxidation by plants, etc., in lakes), or metamorphic (derived from the weathering of rocks).

Metallic manganese.—Impure manganese is obtained by reducing the dioxide with carbon, as described above. If less than the theoretical amount of carbon is used, and the mixture is heated in the electric furnace, a purer metal (nearly free from carbon) is produced: $MnO_2 + 2C = Mn + 2CO$. A purer metal is obtained by reducing the pure dioxide with aluminium in the thermit process (p. 948): $3MnO_2 + 4Al = 2Al_2O_3 + 3Mn$. The purest metal is obtained by electrolysis of a concentrated solution of manganous chloride with a mercury cathode, and distilling of the mercury in a vacuum at 250°.

Manganese is a greyish-white, hard, and brittle metal, sp. gr. 7·4, easily oxidised by air unless it contains iron. It has a high melting point (1245°), but volatilises readily in the electric furnace above 2000°. The metal decomposes water even in the cold, with evolution of hydrogen, and readily dissolves in dilute acids, forming **manganous salts**: $Mn + H_2SO_4 = MnSO_4 + H_2$. It unites directly with nitrogen above 1210°, forming a **nitride**, Mn_5N_3 (Mn_3N_2 is formed by passing ammonia over the heated metal), and with carbon in the electric furnace, forming a soft **carbide**, Mn_3C.

Alloys of iron and manganese, obtained in the blast furnace, are *ferromanganese* (30–80 per cent. of Mn) and *spiegel* (5–20 per cent. of Mn); they are used in making *manganese steel*, which may contain up to 13 per cent. of Mn, and is very hard and tough. It is used for the jaws of rock-crushers, and for machinery. *Manganese bronze* is copper alloyed with 1–2 per cent. of Mn, 8–15 per cent. of Sn, and 0–5 per cent. of Zn. Alloys of copper and zinc with small quantities of manganese resemble German silver. *Manganin* is an alloy of 83 parts of Cu, 13 of Mn, and 4 of Ni. It is used for resistance coils, since its electrical resistance is only slightly affected by temperature after it has been heated repeatedly at 120°. An alloy of 55 of Cu, 15 of Al, and 30 of Mn is magnetic.

Oxides of manganese.—Manganese forms six oxides, the lower oxides being basic, and the higher acidic, which give rise to corresponding series of salts :—

Manganous oxide, $\overset{\mathrm{II}}{\mathrm{Mn}}\mathrm{O}$; strongly basic, forming **manganous salts,** $\overset{\mathrm{II}}{\mathrm{Mn}}\mathrm{SO_4}$.

Mangano-manganic oxide, Mn_3O_4, or $\overset{\mathrm{II}}{\mathrm{Mn}}\mathrm{O},\overset{\mathrm{III}}{\mathrm{Mn}}{}_2\mathrm{O_3}$; a mixed oxide.

Manganic oxide, $\overset{\mathrm{III}}{\mathrm{Mn}}{}_2\mathrm{O_3}$: feebly basic, forming **manganic salts,** $\overset{\mathrm{III}}{\mathrm{Mn}}{}_2\mathrm{(SO_4)_3}$.

Manganese dioxide, $\overset{\mathrm{IV}}{\mathrm{Mn}}\mathrm{O_2}$; feebly acidic, forming **manganites,** $\mathrm{Ca}\overset{\mathrm{IV}}{\mathrm{Mn}}\mathrm{O_3}$.

Manganese trioxide, $\overset{\mathrm{VI}}{\mathrm{Mn}}\mathrm{O_3}$; acidic, forming **manganates,** $\mathrm{K_2}\overset{\mathrm{VI}}{\mathrm{Mn}}\mathrm{O_4}$.

Manganese heptoxide, $\overset{\mathrm{VII}}{\mathrm{Mn}}{}_2\mathrm{O_7}$; acidic, forming **permanganates,** $\mathrm{K}\overset{\mathrm{VII}}{\mathrm{Mn}}\mathrm{O_4}$.

Manganous compounds.—The **manganous salts,** MnX_2, are derived from bivalent manganese, and in solution yield the pale pink cation, $Mn^{\cdot\cdot}$. In the solid state they are pink when water of crystallisation is present.

Manganous chloride, $MnCl_2$.—This salt may be obtained from the residues after the preparation of chlorine from pyrolusite and hydrochloric acid (p. 223) : $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$. Since pyrolusite always contains ferric oxide, the solution is yellow, and contains ferric chloride, $FeCl_3$; this prevents the crystallisation of the manganous chloride on evaporation. In order to separate the iron, one-tenth of the filtered solution which has been evaporated to drive off excess of acid is precipitated with sodium carbonate. Ferric hydroxide and **manganous carbonate,** $MnCO_3$, are thrown down. The precipitate is washed, and added to the remainder of the solution. On boiling, the whole of the iron is precipitated as ferric hydroxide, manganese going into solution, and the filtered solution on evaporation deposits pink monoclinic crystals of $MnCl_2,4H_2O$: $2FeCl_3 + 3MnCO_3 + 3H_2O = 2Fe(OH)_3 + 3MnCl_2 + 3CO_2$.

A hydrate $MnCl_2,6H_2O$, is formed at − 2° ; at 60°, the ordinary form of $MnCl_2,4H_2O$ passes into a second monoclinic form. At 57·85°, $MnCl_2,2H_2O$ is obtained, which at 198° gives rose-red, anhydrous $MnCl_2$. The latter fuses at 650° and volatilises at a higher temperature ; the vapour density is normal.

Manganous carbonate, $MnCO_3$.—By adding sodium carbonate to a solution of a manganous salt, a pale buff-coloured precipitate of

manganous carbonate, $MnCO_3$, is formed, which is soluble in water containing carbon dioxide to form a bicarbonate, and readily oxidises in air when moist to brown manganic hydroxide, $Mn(OH)_3$ (*cf.* $FeCO_3$). It occurs in the bright red mineral *manganese spar*, isomorphous with calcite; the mineral *manganocalcite*, $(Mn,Ca,Mg)CO_3$ is isomorphous with aragonite.

Manganous oxide, MnO.—By heating the carbonate (or any higher oxide of manganese) in hydrogen, **manganous oxide,** MnO, is obtained as a greyish-green powder. If the hydrogen contains a trace of HCl, emerald-green crystals of the oxide MnO are formed. Manganous oxide is also formed on heating the oxalate: $MnC_2O_4 = MnO + CO + CO_2$. If a caustic alkali is added to a solution of a manganese salt, a white precipitate of **manganous hydroxide,** $Mn(OH)_2$, is thrown down, which in presence of air or oxygen rapidly oxidises to brown manganic hydroxide, $Mn(OH)_3$. This reaction is utilised in estimating the oxygen dissolved in water; the precipitate is dissolved in hydrochloric acid, potassium iodide added, and the iodine titrated. One c.c. of $N/10 I_2 = 0{\cdot}0008$ gm. of O_2.

Ammonia only slowly precipitates $Mn(OH)_2$ from a solution containing ammonium chloride. Probably complex ions are formed, but the solution *rapidly* deposits $Mn(OH)_3$ on exposure to air. The usual method of precipitating the metals Fe, Al, Cr by $NH_4Cl + NH_4OH$, and then precipitating Mn in the filtrate with $(NH_4)HS$, is not applicable if the latter metal is present in large amounts.

Manganous sulphide, MnS.—This occurs as the mineral *alabandite.* It is formed as a grey mass by heating the carbonate with sulphur, or as a light flesh-coloured, amorphous powder by precipitating a manganous salt with ammonia and ammonium sulphide. In contact with excess of ammonium sulphide, it passes into a green, crystalline form.

The flesh-coloured form is said to be a mixture of a grey and a red form; if precipitated with sodium sulphide, the grey form is absent, and the precipitate does not become green in contact with excess of reagent.

Manganous sulphide dissolves readily in dilute acids, even acetic; in this way manganese may be separated from zinc, the sulphide of which is insoluble in acetic acid.

Manganous sulphate, $MnSO_4$.—This salt is obtained from pyrolusite by heating with concentrated sulphuric acid: $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$. The residue is heated to redness to decompose ferric sulphate: $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$, dissolved in water, and the filtered solution evaporated. The last traces of iron may be removed by boiling with a little manganous carbonate. The salt forms a number of hydrates: below 8°, $MnSO_4,7H_2O$, isomorphous with $FeSO_4,7H_2O$; at 8–27°, $MnSO_4,5H_2O$, isomorphous with $CuSO_4,5H_2O$; above 27°, $MnSO_4,H_2O$. A labile hydrate, $MnSO_4,4H_2O$, separates out at 30°. Manganous sulphate forms well-crystallised double salts, *e.g.*, $K_2SO_4,MnSO_4,6H_2O$ isomorphous with ferrous ammonium sulphate, $(NH_4)_2SO_4,FeSO_4,6H_2O$.

Manganous ammonium phosphate, $MnNH_4PO_4,H_2O$.—This is formed as a reddish-white, glittering, crystalline precipitate by the addition of ammonium chloride, ammonia, and sodium phosphate to a manganous salt. On ignition, it forms the pyrophosphate, $Mn_2P_2O_7$. This is used in the estimation of manganese.

Manganese carbide, Mn_3C, is formed from the dioxide and excess of carbon in the electric furnace. With water, it yields hydrogen and methane: $Mn_3C + 6H_2O = CH_4 + H_2 + 3Mn(OH)_2$.

Manganous oxalate, $MnC_2O_4,2H_2O$, is obtained as a white, crystalline precipitate. It loses water at 25°.

Manganese borate, $MnH_4(BO_3)_2,H_2O$, is formed as an almost white powder by precipitating manganous sulphate with borax and drying at 100°. At a red heat it forms the metaborate, $Mn(BO_2)_2$. The precipitate is used as a *drier,* for promoting the oxidation of linseed oil in paints and varnishes: it acts catalytically, probably by the intermediate formation of a higher oxide.

Manganic salts, MnX_3.—**Manganic oxide,** Mn_2O_3, occurs in the mineral *braunite*; the **hydroxide,** $Mn(OH)_3$, occurs in the partly dehydrated form as **manganite,** $MnO(OH)$; it is formed as a brown precipitate by passing chlorine through water containing manganous carbonate in suspension. With hot nitric acid it forms manganous nitrate and manganese dioxide: $2MnO(OH) + 2HNO_3 = Mn(NO_3)_2 + MnO_2 + 2H_2O$. **Manganic sulphate,** $Mn_2(SO_4)_3$, is formed as a dark green powder by heating the precipitated dioxide with concentrated sulphuric acid at 138°, draining on a porous tile, washing with concentrated nitric acid, and heating at 150°. It dissolves in water to a violet liquid, which deposits brown hydrated oxide on dilution. It forms alums, *e.g.*, $K_2SO_4,Mn_2(SO_4)_3, 24H_2O$.

Manganic phosphate, $MnPO_4,2H_2O$, is formed as a greenish-grey precipitate when a solution of manganous sulphate containing acetic and phosphoric acids is oxidised by potassium permanganate at 100°. It is insoluble in water, but dissolves in concentrated sulphuric or phosphoric acid to form violet solutions. A violet solution is also obtained by heating a manganous salt with phosphoric and nitric acids at 150°; a lilac precipitate of the **acid pyrophosphate,** $MnHP_2O_7$, is also formed. Manganese salts give a violet microcosmic salt bead.

Manganic chloride, or **manganese trichloride,** $MnCl_3$, is probably contained in the dark brown solution formed when manganese dioxide is dissolved in cold concentrated hydrochloric acid: $2MnO_2 + 8HCl = 2MnCl_3 + 4H_2O + Cl_2$. On warming, chlorine is evolved: $2MnCl_3 = 2MnCl_2 + Cl_2$. The dark brown solution probably also contains the **tetrachloride,** $MnCl_4$: $MnO_2 + 4HCl = MnCl_4 + 2H_2O$. Crystalline double salts of these two higher chlorides are known, *e.g.*, $MnCl_3,2KCl$ and $MnCl_4,2KCl$. If manganese dioxide is suspended in carbon tetrachloride and dry hydrogen chloride passed through, a solid containing $MnCl_3$ and $MnCl_4$ is formed. If the solid is washed with dry ether, a violet solution of **manganese trichloride,** $MnCl_3$, is obtained, and a reddish-brown powder of **manganese tetrachloride,** $MnCl_4$, remains. The tetrachloride forms a red solution in absolute alcohol. Both higher chlorides of manganese are decomposed by water, and the dark brown solution of manganese dioxide in hydrochloric acid also deposits a brown precipitate when poured into water: $MnCl_3 + 3H_2O \rightleftharpoons Mn(OH)_3 + 3HCl$.

Manganese tetrafluoride, MnF_4, on the other hand, is not decomposed by water. It is obtained by dissolving the dioxide in hydrofluoric acid, and forms double salts, *e.g.*, K_2MnF_6.

Mangano-manganic oxide, Mn_3O_4.—This oxide, known as *red oxide of manganese,* occurs in the mineral *hausmannite.* It is formed when any other oxide of manganese is heated strongly in air: $3MnO + O = Mn_3O_4$; $3MnO_2 = Mn_3O_4 + O_2$. It dissolves in cold concentrated sulphuric acid, forming a red solution containing manganous and manganic sulphates: $Mn_3O_4 + 4H_2SO_4 = MnSO_4 + Mn_2(SO_4)_3 + 4H_2O$. Acetic acid gives a solution of manganous acetate and a residue of manganese sesquioxide, Mn_2O_3, hence the red oxide may be regarded as a mixed oxide, MnO,Mn_2O_3, analogous to red lead, or as **manganous manganite,** $Mn(MnO_2)_2$.

Manganese dioxide, MnO_2.—This oxide occurs native as **pyrolusite.** It is prepared in the pure state by heating manganous nitrate until red fumes appear, decanting the clear liquid from the residue of lower oxides, and heating it for forty to sixty hours at 150–160°. If solutions of manganous salts are treated with oxidising agents such as potassium permanganate, sodium hypochlorite, ammonia and bromine, or ozone, brown precipitates are obtained, which on washing form brown colloidal solutions. These precipitates, however, always contain less oxygen than corresponds with the formula MnO_2. Manganese dioxide is a feebly acidic oxide, and with strong bases forms salts called **manganites,** *e.g.*, CaO,MnO_2 and $CaO,2MnO_2$ (see Mn_3O_4).

The commercial dioxide is used as an **oxidising agent,** and may be analysed as follows: (1) The solid is boiled with a standard solution of oxalic acid, containing sulphuric acid. A portion of the oxalic acid is oxidised: $C_2H_2O_4 + MnO_2 + H_2SO_4 = 2CO_2 + MnSO_4 + 2H_2O$. The excess of oxalic acid is then titrated with potassium permanganate solution. (2) The oxide is heated with concentrated hydrochloric acid in a small flask, and the chlorine evolved passed into a solution of potassium iodide contained in a U-tube cooled by water. Iodine is liberated, which is titrated with standard sodium thiosulphate solution. (3) The dioxide is boiled with an acidified solution of standard ferrous sulphate in a flask fitted with a tube dipping under water to exclude air. The excess of ferrous sulphate is titrated with standard permanganate solution: $MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$ The first method usually gives the most accurate results.

Manganic disulphate, $Mn(SO_4)_2$, corresponding with manganese dioxide, is obtained in black crystals or a deep brown solution by the electrolysis of a solution of manganous sulphate in fairly concentrated sulphuric acid with a platinum anode. It is used as an oxidising agent.

Besides its use in decolorising glass, manganese dioxide is applied, mixed with ferric oxide, as a dark brown glaze to pottery. It is also used as a depolariser in the **Leclanché cell.**

In the simplest form this consists of a rod of amalgamated zinc immersed in a concentrated solution of ammonium chloride, in which is also placed a porous pot containing a rod of gas carbon surrounded by a granular mixture of crushed pyrolusite and gas carbon. In a second form, the pyrolusite is formed into blocks, one of which is placed on each side of a gas-carbon plate, being held in position by rubber bands. In the **dry cell,** used in enormous numbers for portable lamps and other purposes, the ammonium chloride solution is gelatinised by adding glue, the gas-carbon rod is surrounded by a gelatinised paste of manganese dioxide and ammonium chloride, and the zinc pole consists of a zinc cylinder containing the materials of the cell.

The reaction in the cell is the solution of zinc to form a double chloride: $Zn + 5NH_4Cl = ZnCl_2,3NH_4Cl + 2NH_3 + H_2$. The hydrogen is deposited on the pyrolusite, and is oxidised by the trace of manganic ions formed by the minute amount of the manganese dioxide in solution:

$$\begin{aligned}
&MnO_2\ (\text{solid}) + \text{Aq.} \rightleftarrows Mn(OH)_4\ (\text{dissd.}) \rightleftharpoons Mn^{::} + 4OH'.\\
&Mn^{::} + H + OH' \rightleftarrows Mn^{\cdot\cdot\cdot} + H_2O.\\
&Mn^{\cdot\cdot\cdot} + 3OH' \rightleftharpoons Mn(OH)_3\ (\text{dissd.}) \rightleftharpoons Mn(OH)_3\ (\text{ppd.})
\end{aligned}$$

The compound $ZnCl_2,3NH_4Cl$ slowly separates in crystals on the zinc rod.

The cell rapidly polarises, since the concentration of depolarising $Mn^{::}$ ions is small, but recovers fairly quickly on standing, when more MnO_2 goes into solution. It is useful when intermittent currents of short duration are required, as in operating bells or flash-lamps.

Manganates and permanganates.—If manganese dioxide is fused with caustic soda or potash with free access to air, a green mass is formed which contains a **manganate,** *e.g.*, K_2MnO_4. The reaction is more complete with caustic potash (2·4 mols. to 1 mol. of MnO_2) and more rapid if potassium or sodium nitrate or chlorate is added to the alkali: $4KOH + 2MnO_2 + O_2 = 2K_2MnO_4 + 2H_2O$. The dark green mass may be dissolved in a small quantity of cold water, forming a dark green solution, from which on evaporation in a vacuum dark green crystals of the manganates, K_2MnO_4, or $Na_2MnO_4,10H_2O$, are deposited. These are isomorphous with the corresponding sulphates, K_2SO_4 and $NaSO_4,10H_2O$. Sodium manganate is used as a disinfectant, since it is a powerful oxidising agent.

If the dark green solution of the manganate in a little water is poured into a large volume of water, a purple solution of **permanganate** and a brown precipitate of hydrated manganese dioxide are formed: $3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KOH + MnO_2$. In presence of a large excess of alkali, the reaction does not take place, and the manganate is stable. The reaction occurs completely if the alkali produced is removed by adding an acid; even carbonic acid is effective. If a *pure* alkali is added to the purple solution of permanganate, no reaction occurs, but as commercial alkali always contains nitrites, which are readily oxidised, this causes the colour to change again to green: $2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + O$. With very concentrated solutions of permanganate and pure alkali, however, this reaction occurs spontaneously, and oxygen gas is evolved.

The formation of manganates and permanganates by the above reactions was discovered by Glauber in 1656; on account of the colour changes which it undergoes the manganate was called *mineral chamelion* by Scheele. The salts were investigated by Forchhammer in 1820 and by Mitscherlich in 1832. The latter showed that the green and purple salts were derived from two distinct acids, **manganic acid**, H_2MnO_4, and **permanganic acid**, $HMnO_4$, and that the salts are isomorphous with sulphates and perchlorates, respectively. Potassium permanganate may be obtained from the manganate by passing chlorine through the solution: $2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$.

Permanganic acid, $HMnO_4$.—Manganic acid is not known in the free state, since manganates, when treated with other acids, do not give manganic acid but permanganates. **Permanganic acid,** $HMnO_4$, is obtained in solution by boiling a solution of manganous sulphate with lead dioxide and nitric acid. If a solution of silver nitrate and potassium permanganate is crystallised, **silver permanganate,** $AgMnO_4$, is obtained. If this is decomposed with barium chloride, **barium permanganate**, $Ba(MnO_4)_2$, is obtained, which, when treated with dilute sulphuric acid, gives a purple solution of permanganic acid, violet crystals of which are formed by evaporation in a vacuum. The acid is unstable; the solution rapidly decomposes with evolution of oxygen and deposition of manganese dioxide: $4HMnO_4 = 4MnO_2 + 2H_2O + 3O_2$. It is a powerful oxidising agent.

Manganese heptoxide, or permanganic anhydride, Mn_2O_7.—When powdered potassium permanganate is added in small quantities at a time to cooled concentrated sulphuric acid, a dark green solution is formed, which appears to contain the sulphate of manganese trioxide, $(MnO_3)_2SO_4$, or Mn_2O_7,SO_3. This green liquid is liable to explode violently in contact with traces of organic matter, or even spontaneously. When treated with ice-cold water, dark oily drops of **manganese heptoxide**, Mn_2O_7, the anhydride of permanganic acid, separate :

$$\begin{aligned} 2KMnO_4 + 2H_2SO_4 &= (MnO_3)_2SO_4 + K_2SO_4 + 2H_2O. \\ (MnO_3)_2SO_4 + H_2O &= Mn_2O_7 + H_2SO_4. \end{aligned}$$

Manganese heptoxide is an opaque, oily liquid, sp. gr. 2·4, which forms a violet vapour at 40–50°, but explodes violently on warming or in presence of organic matter. It dissolves unchanged in glacial acetic acid.

If fused sodium chloride is added to the green solution of potassium permanganate in concentrated sulphuric acid, a yellow gas is evolved which condenses in a freezing mixture to a greenish-brown liquid, **permanganyl chloride**, MnO_3Cl, the acid chloride of permanganic acid. It explodes on heating, and in moist air emits purple fumes, owing to hydrolysis into hydrochloric and permanganic acids. The same reaction occurs in presence of water, but the two acids mutually decompose each other, with formation of hydrochloric acid and manganese dioxide. The corresponding **fluoride**, MnO_3F, has been prepared.

The oxide MnO_3 has been described, but its existence is doubtful. It is said to be formed by dropping the green solution of $KMnO_4$ in H_2SO_4 on dry sodium carbonate, but the purple fumes evolved are more probably permanganic acid droplets, formed from the water produced by the interaction of H_2SO_4 and Na_2CO_3.

Potassium permanganate, $KMnO_4$.—This important salt is made by fusing manganese dioxide with caustic potash and potassium nitrate or chlorate, boiling the green mass of manganate with water, filtering the solution through asbestos, and passing a current of carbon dioxide through the solution. A purple solution of potassium permanganate is formed : $3K_2MnO_4 + 2H_2O + 4CO_2 = 2KMnO_4 + MnO_2 + 4KHCO_3$. The solution is again filtered through asbestos or glass-wool, and evaporated. Deep purple-red, brilliant rhombic prisms of the permanganate separate. These have a green iridescence and dissolve in water (4·4 in 100 at 10° ; 5·31 at 15° ; 32·4 at 75°) to a deep purple solution, which is opaque unless dilute. The crystals evolve oxygen on heating and fall to a black powder : $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$. At a red heat the manganate is also decomposed, with evolution of oxygen.

Potassium permanganate is also manufactured from the manganate by the electrolytic oxidation of the solution between iron or nickel electrodes. If an electrode of manganese or ferromanganese is made the anode in a solution of caustic potash, and a nickel cathode used, a solution of the permanganate may be obtained directly, but the yield is small.

Calcium permanganate, $Ca(MnO_4)_2$, is manufactured by the addition of chalk to a solution of permanganic acid obtained by electrolytic oxidation of a manganous salt. It is a deep violet, hygroscopic powder, readily soluble in water, and is used in sterilising water. It loses oxygen more readily than the potassium salt.

Potassium permanaganate is a **powerful oxidising agent**. It burns violently when mixed with sulphur or charcoal and ignited. The oxidising action is different according as the reaction is carried out in alkaline or in acid solution.

(1) In **alkaline solution**, in the presence of reducing agents, the permanganate is first reduced to green manganate. The solution then deposits brown manganese dioxide and becomes colourless. The reactions are :

$$\begin{aligned} 2KMnO_4 + 2KOH &= 2K_2MnO_4 + H_2O + O. \\ 2K_2MnO_4 + 2H_2O &= 2MnO_2 + 4KOH + 2O. \end{aligned}$$

Hence, two molecules of potassium permanganate in alkaline solution give *three* atoms of available oxygen when reduced to manganese dioxide. The reaction may also be represented in the dualistic notation (p. 275) as follows :

$$2KMnO_4 = K_2O,Mn_2O_7 = K_2O + 2MnO_2 + 3O.$$

Expt. 334.—Add a little sugar solution to an alkaline solution of potassium permanganate and warm. Observe the change of colour to green, followed by the discharge of colour and the formation of a brown precipitate.

Alkaline permanganate oxidises an iodide to an iodate :

$$2KMnO_4 + H_2O + KI = 2MnO_2 + 2KOH + KIO_3.$$

A manganous salt is oxidised in *neutral* solution to manganous manganite :

$$\begin{aligned} 4KMnO_4 + 11MnSO_4 + 14H_2O &= \\ &4KHSO_4 + 7H_2SO_4 + 5Mn(HMnO_3)_2. \end{aligned}$$

(2) In *acid solutions*, the permanganate is reduced to a manganous salt and *five* atoms of oxygen become available from two molecules of permanganate :

$$\begin{aligned} 2KMnO_4 + 3H_2SO_4 &= K_2SO_4 + 2HMnO_4 + H_2O + 2H_2SO_4. \\ &= K_2SO_4 + 2MnSO_4 + 3H_2O + 5O ; \end{aligned}$$

or, in dualistic notation :

$$2KMnO_4 = K_2O,Mn_2O_7 = K_2O + 2MnO + 5O.$$

In acid solutions, iodine is liberated from **potassium iodide**:

$$2KMnO_4 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O.$$

Ferrous salts are oxidised to ferric salts:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

Oxalic acid is oxidised to carbon dioxide:

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

Nitrites are oxidised to nitrates:

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3.$$

Sulphur dioxide is oxidised to sulphuric acid:

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 3H_2SO_4.$$

The reaction with **hydrogen peroxide** has been described (p. 162). The reactions are accelerated by the presence of manganous salts, which act catalytically.

EXPT. 335.—To a solution of oxalic acid acidified with sulphuric acid and warmed at 60°, add potassium permanganate solution from a burette. With the first few c.c. the colour is discharged only slowly, but as manganous sulphate accumulates, the colour is quickly discharged.

In **volumetric analysis**, solutions of potassium permanganate are made up according to the content of **available oxygen.** A **normal solution** is one containing one gram equivalent of active substance per litre. In the case of permanganate this will be 7·94 gm. of available oxygen. The solubility of the salt is not sufficient to give a normal solution, so that semi-normal ($N/2$) and decinormal ($N/10$) solutions are used. $2KMnO_4$ give $5O$ $\therefore$ a normal solution will contain $\frac{2KMnO_4}{5 \times 2}$ gm., and a decinormal solution $\frac{2KMnO_4}{5 \times 2 \times 10} = 3{\cdot}137$ gm. per litre. The solution may be standardised by oxalic acid. In the oxidation of ferrous salts, $2FeO$ require $3O$ to form Fe_2O_3, or 55·4 gm. of iron require 7·94 gm. of oxygen; hence 1 c.c. of $N/10 KMnO_4 =$ 0·00554 gm. of Fe.

Cyanogen compounds.—Potassium cyanide gives with solutions of manganous salts a yellowish-grey precipitate of **manganous cyanide,** $Mn(CN)_2$. This is soluble in excess of the reagent, giving a yellow solution of **potassium manganocyanide,** $K_4Mn(CN)_6$, analogous to the ferrocyanide, which crystallises as a deep blue solid, $K_4Mn(CN)_6,3H_2O$. By evaporating this solution in air, a portion of the manganese is oxidised and precipitated, and the solution contains **potassium manganicyanide,** $K_3Mn(CN)_6$. This forms large red prisms. The resemblance between manganese and iron is apparent: the corresponding salts are isomorphous.

EXERCISES ON CHAPTER XLVII

1. Discuss the position of manganese in the Periodic System. What analogies does it show to iron and chromium ?

2. How are the oxides of manganese prepared, and what are their properties ? How is the available oxygen in manganese dioxide estimated ?

3. Describe the preparation of a pure manganous salt from pyrolusite.

4. How is manganous sulphide prepared, and what are its properties ?

5. Describe the preparation of potassium permanganate. Give examples of its action as an oxidising agent. How would you determine the strength of a solution of hydrogen peroxide by means of potassium permanganate ?

6. How are the following obtained : (*a*) manganese trichloride, (*b*) potassium manganocyanide, (*c*) manganese pyrophosphate, (*d*) manganese heptoxide ?

CHAPTER XLVIII

IRON

The transitional elements.—The eighth group of the Periodic System comprises three sub-groups, with three elements in each, forming the termination of the even series 4, 6, and 8, and connecting the elements of these series with those of the odd series following. For this reason they were called by Mendeléeff the *transitional elements* :

Group A : Iron, 55·40 ; Cobalt, 58·50 ; Nickel, 58·21.
Group B : Ruthenium, 100·9 ; Rhodium, 102·1 ; Palladium, 105·9.
Group C : Osmium, 189·4 ; Iridium, 191·6 ; Platinum, 193·6.

The propriety of separating these elements from the rest and placing them in a special group is justified by their peculiar properties. The **atomic weights** of the members of each of the three groups differ so little from one another that the three elements may be regarded as forming a single cluster which takes the place of a single element in the other groups of the Periodic System. A similar behaviour is shown by the rare-earth elements (p. 461).

The physical and chemical properties of the elements are also closely related ; *e.g.*, the platinum metals of groups B and C are very similar ; they are difficult to separate, as are also cobalt and nickel. The elements in the vertical columns show close resemblances ; ruthenium and osmium form higher oxides, RO_4 ; rhodium and iridium, palladium and platinum also exhibit analogies. The resemblance between the metals of the iron group and the platinum metals is, however, somewhat remote, and is chiefly confined to the facility with which all the metals of Group VIII form **complex compounds** :

potassium ferrocyanide, $K_4Fe(CN)_6$;	potassium cobaltinitrite, $K_3Co(NO_2)_6$;
potassium chloroplatinate, K_2PtCl_6 ;	sodium osmichloride, $Na_2OsCl_6,2H_2O$

Nickel shows this property to a much smaller degree. The platinum metals, both in their physical properties, *e.g.*, their "noble" character, and their tendency to complex-formation, closely resemble gold, which follows them in the periodic table. All the elements of Group VIII, unlike the other members of *even series*, form organo-metallic compounds.

The typical **oxide** of these elements should be, according to their position in the Periodic System, RO_4, but this is confined to ruthenium and osmium. All the elements form lower, basic oxides.

The elements of the **iron group**: **iron, cobalt,** and **nickel,** are magnetic metals with high melting points, which oxidise in the air at a red heat, and decompose steam at high temperatures. The oxides $\overset{II}{R}O$ are all known, and strong bases. The sesquioxides, $\overset{III}{R_2}O_3$, are also basic, but their salts are stable only in the case of iron. Oxides of the type R_3O_4 are also known; their salts, if they exist, are very unstable, so that these oxides probably have the formula $\overset{II}{R}O, \overset{III}{R_2}O_3$, or $R(RO_2)_2$, in which R_2O_3 functions as a feebly acidic oxide, and RO as a base. Compounds such as CaO,Fe_2O_3, or $Ca(FeO_2)_2$ **(ferrites)**, are known. Iron forms compounds of an unknown acidic trioxide, FeO_3, *e.g.*, **potassium ferrate** K_2FeO_4, in which the element shows a resemblance to manganese and chromium, which form K_2MnO_4 and K_2CrO_4. The metals iron, manganese, and chromium are also similar in their physical properties.

The elements of Group VIII all form compounds, called **carbonyls** with carbon monoxide; *e.g.*, $Ni(CO_4)$. Molybdenum forms a carbonyl. In these compounds the metal appears to function with its maximum valency:

Iron. $Fe = 55{\cdot}40$.

Iron.—The element **iron,** by reason both of its abundant occurrence and of its manifold uses, is undoubtedly the most important of the metals. On account of its high melting point and the comparative difficulty with which iron is reduced from its ores, the metal was probably not known until a later period (*c.* B.C. 1500) than bronze (*c.* B.C. 3000), although the more permanent character of the latter metal may be the reason why the bronze implements of prehistoric man have persisted, whilst iron, if it existed at all, has rusted away and disappeared. It was certainly regarded by the ancients as a rarity, since Homer refers to the prize of a ball of iron awarded to Achilles for his athletic skill. From its obvious association with military exploits, the alchemists named the metal after the planet Mars and denoted it by the symbol of the spear and shield : ♂.

Iron does not occur to any great extent in the free state on the earth, although **meteorites,** which consist of metallic iron with from 3 to 30 per cent. of nickel, indicate that it must be present in the solar system. Meteorites may consist partly of silicates (*e.g.*, olivine), and of glassy minerals (moldavite). On account of the presence of nickel, meteoric iron does not easily rust in moist air. Meteoric dust, consisting chiefly of iron, is constantly falling on the earth from space, although its presence is only noticed on the surface of the otherwise unsullied snows of the polar regions. Large masses of **native iron,** which may be of meteoric origin, or have been derived from the reduction of ores in burning coal-mines, occur in many localities, particularly at Disko Island, West Greenland. Metallic iron also occurs in grains in basalt rocks, found at Giant's Causeway, and elsewhere. Iron is contained in the chlorophyll of green plants, and in hæmoglobin (0·336 per cent. Fe), the red colouring matter of blood.

Iron ores.—The **ores of iron** are plentiful but relatively few in number, although the element occurs in nearly every mineral, in rocks, and in soils. The most important ores are the **oxides.** The black oxide, Fe_3O_4, or **ferroso-ferric oxide,** occurs as the important ore **magnetite,** so-called because certain varieties (lodestone) are permanently magnetic. This ore is not found to any extent in the British Isles, but occurs in Lapland, Sweden, Siberia, Germany, and North America. It contains 72·4 per cent. of iron, and is the richest ore of the metal. The **sesquioxide,** Fe_2O_3, occurs as *hæmatite,* which is crystalline and has a red colour, or if black, as is sometimes the case, gives a red streak when drawn over an unglazed porcelain plate. It is found in Belgium, Sweden, the Island of Elba, south of Lake Superior, and in England in the Furness district in Lancashire. The **hydrated sesquioxide,** $2Fe_2O_3,3H_2O$, *limonite,* occurs in kidney-shaped amorphous masses in South Wales, the Forest of Dean, and at Bilbao in Spain. The so-called *bog iron ores* are hydrated oxides, and occur in large quantities in Ireland, Sweden, and North Germany. The only remaining important ore is ferrous carbonate, $FeCO_3$, occurring either alone, as *siderite, chalybite,* or *spathic iron ore,* or mixed with clay as *clay-ironstone,* or with clay and coal as *blackband-ironstone.* The hydrated oxide and the impure forms of the carbonate are the most important British ores.

Pyrites cinders, chiefly ferric oxide, from the manufacture of sulphuric acid (p. 503) are desulphurised by roasting and smelted for iron.

The value of an ore of iron depends on its freedom from impurities (S, P, As, etc.), which are detrimental to the resulting metal. Three varieties of commercial iron are made: (1) **cast-iron,** or pig-iron; (2) **malleable iron,** or wrought-iron; (3) **steel.**

The metallurgy of iron.—The order in which the varieties of iron are prepared from the ore is roughly as follows:

↗ **Wrought-iron → Crucible Steel.**
Ore → Cast, or **Pig-iron**
↘ **Bessemer,** or **Open-hearth Steel.**

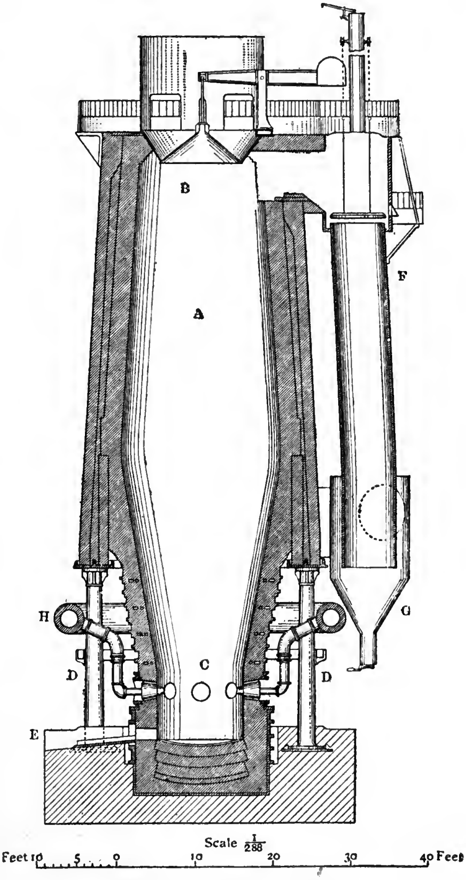


Fig. 420.—Blast Furnace.

The extraction of iron from the ore involves a number of processes.

(1) **preliminary roasting,** or calcination, to drive off carbon dioxide and moisture and leave ferric oxide, Fe_2O_3. This operation is carried out by stacking the ore with a little coal in heaps or in shallow kilns, and regulating the temperature and supply of air so that most of the moisture, carbon dioxide, sulphur, and arsenic are expelled; ferrous oxide (FeO) is also converted into ferric oxide (Fe_2O_3), to avoid the production of ferrous silicate in the slag during smelting. The ore is also rendered more porous.

(2) **Smelting,** or reducing the ore with carbon in the **blast-furnace.**

The blast-furnace.—The **blast-furnace,** introduced about 1500 (Fig. 420) consists of an outer shell of steel plates, lined with refractory bricks. It is 50–100 ft. high, the greatest width being about 24 ft. (at the "boshes"). The mouth is closed with a *cup-and-cone, B,* through which a mixture of ore and fuel is fed intermittently into the furnace, whilst the gases (carbon monoxide and nitrogen) pass away through the pipe, *F*, to a *dust-catcher*, *G*, and are utilised in heating the blast. The furnace below the *boshes* narrows gradually to a *hearth*, *C*, at the base, about 10 ft. in diameter, and the same height. This is pierced with holes for the water-jacketed iron blowing-pipes, or *tuyeres*, through which air is forced from the annular pipe, *H*, by means of powerful blowing engines. The hearth is also pierced with a hole, *E*, from which the molten iron is periodically tapped into sand moulds on the ground, and a *slag-notch* (not shown in the figure) at a higher level, through which the molten slag runs continuously from above the fused metal. About 3–4 tons of air are passed through the furnace per ton of iron made, the power for working the blowing-engines being supplied by coke-oven gas obtained in producing the coke for the blast furnace.

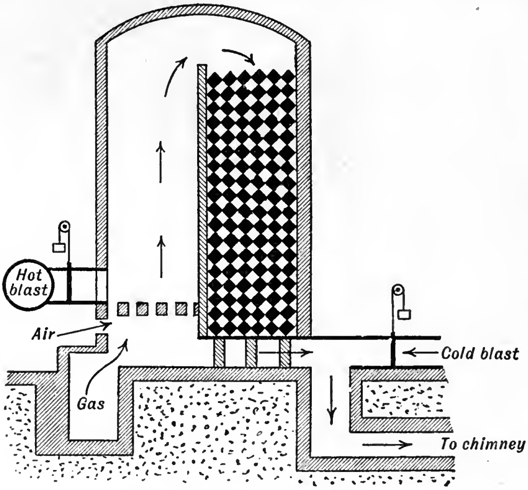


FIG. 421.—Cowper Stove.

The **charge** for the blast-furnace consists of 1 ton of hard oven-coke and 8–12 cwt. of limestone (to form the slag, consisting of calcium and aluminium silicates) to so much ore (say $2\frac{1}{2}$ tons) as produces 1 ton of iron. The process is continuous and goes on for years without interruption. The furnace should not be allowed to cool, when a hard mass of slag and metal would be produced, which has to be blasted out and the furnace re-started, an operation lasting some months. Each furnace may produce 1000–1300 tons of cast-iron per week.

The air blast has since 1828 been pre-heated to 700–800°. This **hot blast** is now produced by passing the air through **Cowper stoves** (Fig. 421), consisting of tall iron cylinders lined with firebricks, packed on one side with chequer brickwork. Part of the hot gas from the blast furnace, together with sufficient air to burn it, passes through these until the bricks are heated to redness. The gas is then turned through a second stove and the air blast to the tuyeres sent through the first one until the brickwork has cooled. The two stoves are thus alternately used as absorbers and emitters of heat, or as **heat-regenerators.** In this way an economy of fuel is effected, and the furnace works at a higher temperature. The normal composition of blast-furnace gas, by volume, is: N_2, 60; CO, 24; CO, 12; H_2 and CH_4, 4.

In some cases a *dry blast* is used, the air passed through the Cowper stoves being first cooled by refrigeration to remove moisture. In this way loss of heat by the reaction: $C + H_2O \rightleftharpoons CO + H_2$, in the blast furnace, is said to be prevented. The furnace gases, after cooling by passing through long iron pipes sprayed with water, are *filtered* through cloth bags, or treated by electrostatic precipitation, to remove dust, which may be rich in potassium salts. If coal is used in the furnaces the cooled gases are scrubbed with water to recover the ammonia.

Chemical reactions in the blast furnace.—The oxygen of the blast unites with carbon in the hearth to produce **carbon monoxide**: (1)$2C + O_2 \rightleftharpoons 2CO$. The temperature of the charge passing down the furnace increases continually from the mouth to the hearth. The reactions in different parts of the furnace, starting at the mouth, will now be considered.

Above the boshes, at a dull red-heat (500–900°), the ferric oxide is reduced by the carbon monoxide to spongy iron:

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2.$$

The reaction is reversible, and the escaping gases contain CO and CO_2 in the ratio 1 to 0·5. Two other reactions also occur, which limit the completeness of the reduction: $2Fe + CO_2 \rightleftharpoons Fe_2O_3 + CO$, and $2Fe + 3CO \rightleftharpoons Fe_2O_3 + 3C$.

In this upper zone the limestone is decomposed: $CaCO_3 \rightleftharpoons CaO + CO_2$, and some carbon dioxide is reduced to monoxide: $CO + C \rightleftharpoons 2CO$. The spongy iron absorbs sulphur from the fuel.

Near the centre of the furnace, at a bright red heat, finely-divided carbon is deposited by the reaction: $2CO \rightleftharpoons CO_2 + C$; phosphorus is produced by reduction of phosphates in the ore: $P_2O_5 + 5Fe + 5SiO_2 = 5FeSiO_3 + 2P$, and alloys with the iron. At a higher temperature silicon is formed by reduction of silicates with iron and carbon, and alloys with the iron, whilst a portion of the silica unites with bases (CaO,Al_2O_3) to form a fusible slag.

At a white heat in the lowest part of the furnace the spongy iron, containing carbon, sulphur, phosphorus, and silicon, fuses to molten cast-iron, which is tapped off from time to time into sand moulds to form pig-iron, or is sent in the fused state to the steel furnaces. The heat evolved in the main reaction is: $Fe_2O_3 + 3CO = 2Fe + 3CO_2 + 8{\cdot}65$ kg. cal.

Cast-iron.—*Pig-iron* contains from 3 to 4 per cent. of carbon, together with silicon, sulphur, phosphorus, and manganese. When the cooling is rapid, the silicon content small, and the manganese high, *white pig-iron* is formed, in which all the carbon is in the form of iron carbide, Fe_3C (**cementite**). It is brittle, coarsely crystalline, and dissolves nearly completely in dilute hydrochloric acid, evolving a mixture of hydrogen and hydrocarbons. If, however, the molten iron containing at least 2·5 per cent. of silicon is *slowly* cooled, most of the carbon separates in the form of fine laminæ of *graphite*, the metal at the same time becoming softer and of a finer texture; on solution in hydrochloric acid it evolves chiefly hydrogen and leaves a black residue of graphite. This variety of cast-iron is known as *grey pig-iron*. An intermediate variety is called *mottled pig-iron*. The solubility of carbon in pure iron is 4·5 per cent.; much more is dissolved if manganese is present.

Malleable, or wrought, iron.—This variety is nearly pure iron, containing only from 0·12 to 0·25 per cent. of carbon, and melts at a higher temperature (1400–1500°) than cast-iron. Malleable iron contains less than 0·5 per cent. of total impurities (carbon, sulphur, phosphorus, silicon).

Malleable iron is obtained from cast-iron by the **puddling process,** invented by Cort in 1784. The cast-iron is fused in a reverberatory furnace, the hearth of which is lined with hæmatite, which oxidises the carbon: $3C + Fe_2O_3 = 2Fe + 3CO$, the carbon monoxide bubbling through the molten iron. Sulphur, phosphorus, and silicon are oxidised and pass into the slag. When the metal becomes pasty it is formed into lumps, or "blooms," which are beaten under steam hammers to squeeze out the slag.

The iron, although not fused, *welds* together to a coherent mass at about 600°. Malleable iron is tough and fibrous; its property of welding, whereby two pieces when heated to redness unite on hammering, is exceedingly valuable and is applied in various ways by the blacksmith. Its softness is not appreciably altered by heating to redness and quenching in water, whereas steel then becomes very hard.

If wrought iron contains combined phosphorus, it is brittle at the ordinary temperature, and is said to be *cold-short*; combined sulphur, probably FeS, renders the metal brittle at a red heat, when it is known as *red-short*.

Steel.—**Steel** is iron which has been fused in the process of manufacture and contains 0·15 to 1·5 per cent. of combined carbon dissolved in the form of cementite, Fe_3C. It may also contain manganese, titanium, chromium, nickel, tungsten, and vanadium. Steel may be made (1) from cast-iron by removing part of the carbon, (2) from wrought-iron by adding combined carbon.

Before Cort's discovery, wrought-iron was made from pure oxide ores by reduction with charcoal and was converted into steel by the

cementation process. Bars of wrought-iron are heated with charcoal for one or two weeks. Absorption of carbon gradually occurs, the carbonisation spreading slowly through the mass, and converting the iron into steel. The surface of the bars is covered with blisters, and the "blister steel" is fused in plumbago crucibles to form cast-steel or **crucible steel.** The addition of **spiegel,** an alloy of iron, carbon, and manganese, to the molten steel improves its quality. The mechanism of the absorption of carbon by iron is not very clear. It is stated that pure carbon, free from gases, does not penetrate iron except under high pressure, so that carbon monoxide may be the active agent. Unstable **iron carbonyls** may be formed as intermediate products (p. 992).

Modern steel is produced by removing part of the carbon of cast-iron by:

(1) **The Bessemer process** (Kelly, 1852; Henry Bessemer, 1855).

(2) **The Open-hearth process (Siemens-Martin process,** W. Siemens, 1863, and E. Martin, 1864).

The Bessemer process.—This process is, after Cort's discovery, one of the master-processes in the metallurgy of steel. The molten iron from the blast furnaces is run into a **converter** (Fig. 422), a large pear-shaped iron vessel, *A*, lined with refractory silica bricks, *C*. The converter holds 10 tons of metal, and is supported on trunnions, air being led by a pipe, *D*, to a hollow perforated bottom, *M*, from which it is forced through the metal. The charging with molten cast-iron is carried out through the open mouth with the converter in a horizontal position, and blowing is then begun. The converter is next swung into a vertical position, and the blowing continued. Silicon is first oxidised to silica which passes into the slag, then a portion of the iron is oxidised. The resulting ferric oxide removes the carbon, forming carbon monoxide, which is freely evolved from the molten iron and burns at the mouth of the converter as an orange-yellow flame edged with blue, shot through by showers of sparks. After six to eight minutes the flame sinks, indicating that the carbon has been removed. The converter is again tilted, the blast stopped, and the requisite amount of spiegel added—a method of carburising the metal introduced by Mushet in 1856. The molten steel is poured, by further tilting the converter, into ladles supported by travelling cranes, from which it is run into moulds. A little silicon-iron alloy (*silicon-spiegel*), or titanium-iron alloy, may be added to remove blow-holes in the castings due to bubbles of gas, which combine with the silicon or titanium (O_2, N_2, CO). According to the percentage of carbon added, various kinds of steel are produced: **tool steel** (0·9–1·5 per cent. C); **structural steel** (0·2–0·6 per cent. C); **mild steel** (0·2 per cent., or less, C). Special steels are produced by adding alloys of iron with tungsten, chromium, molybdenum, and vanadium; or nickel.

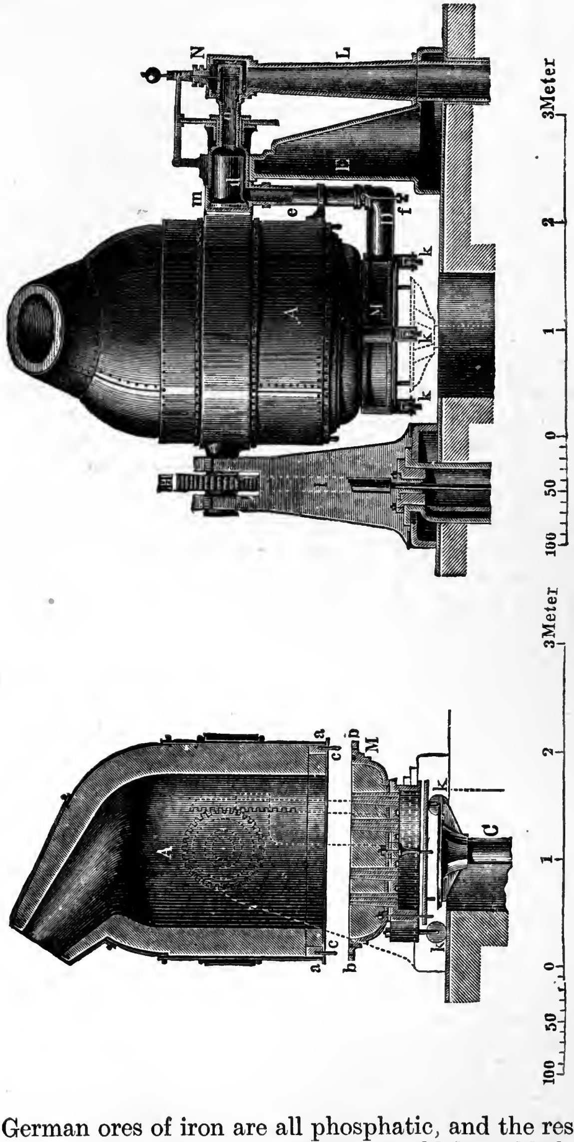


FIG. 422.—Bessemer Converter.

The German ores of iron are all phosphatic, and the resulting iron or steel, if made in the ordinary way, would be cold-short. Such "phosphatic ores" may be worked by the process of Thomas and

Gilchrist (1879), in which the silica (" acidic ") lining of the converter is replaced by a " basic " lining of magnesia and lime, prepared by calcining dolomite. Limestone is first charged into the converter, along with coke, and the blast turned on. Molten pig-iron is then run in and the blast continued. Carbon is first burnt out as usual, but if the blast is prolonged after the flame drops the phosphorus is oxidised, unites with the lime and forms a slag containing calcium phosphate and free lime (**basic slag,** or **Thomas slag**), which is a valuable fertiliser. Spiegel is then added to form the steel. In this way it is possible to treat pig-iron containing as much as 3 per cent. of phosphorus. The steel pigs produced by casting are annealed in underground furnaces (" soaking-pits ") heated by blast-furnace gas, and are then passed through the rolling mills for the production of steel bars.

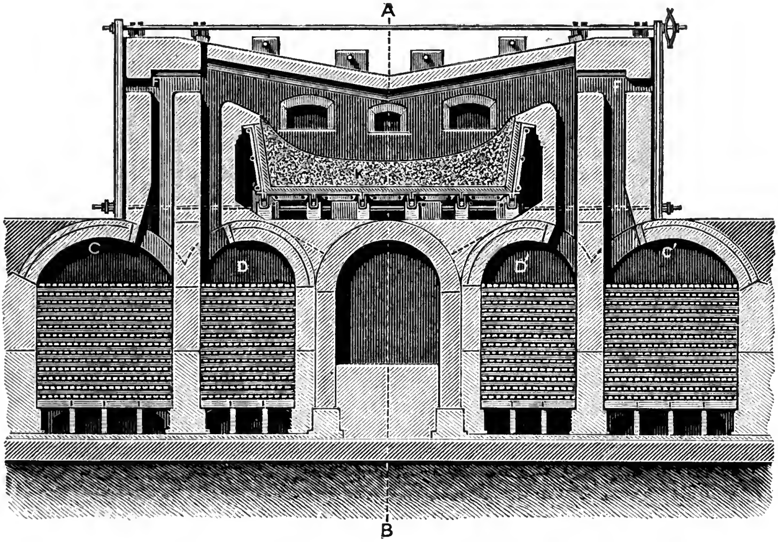


FIG. 423.—Siemens-Martin Process.

The open-hearth process.—The **open-hearth process** is carried out in a large flat crucible enclosed in a furnace (Fig. 423) heated by producer gas. The air and gas are supplied through separate regenerators of chequer brickwork, used in pairs and alternately traversed by the hot products of combustion and the gases, as in the case of Cowper stoves (p. 976). Molten cast-iron from the blast-furnace is run on the hearth, which is lined with ganister in the acid process or calcined magnesite or dolomite in the basic process. The requisite amount of hæmatite, Fe_2O_3, is then added, so that a portion of the carbon is burnt out of the cast-iron and fluid steel remains. The subsequent operations are the same as in the Bessemer process. The furnace may be made to tilt and discharge a portion of its contents into the ladle. The operation lasts 8–10 hours; it is more easily controlled than the Bessemer process, and is very largely used.

Electric furnaces are used in the production of special high-quality steels. They are mostly on the arc principle, and consist of refractory crucibles containing two (or more) large carbon electrodes between which an electric arc is struck.

In 1917, the total output of steel was 75,000,000 tons, of which 42,000,000 tons were produced in the United States of America.

The properties of steel.—The properties of steel depend largely on the content of carbon: low-carbon steels are soft, like wrought-iron, and are known as **mild-steel**; with further addition of carbon the ductility falls, whilst the tensile strength increases up to the limiting percentage of 1·5 C. Cast-iron has a tensile strength of 10 tons per sq. in., wrought-iron of 25 tons, and steel of 30–40 tons. Wrought-iron and steel are highly malleable and may be welded. The melting-point of steel is lower than that of wrought-iron. The properties of steel depend also on the *heat-treatment* to which the metal has been subjected. If steel is heated to redness and plunged into cold water it becomes as hard and brittle as glass. If it is now heated to various temperatures, the resulting metal possesses properties depending on the temperature. This operation is known as **tempering**, and the temperature is judged by the colour of the thin film of oxide produced on a bright surface of the metal:

230°: light straw colour: used for razor blades.
255°: brownish-yellow: used for penknives and axes.
277°: purple: used for cutlery.
288°: bright blue: used for watch-springs and swords.
290-316°: dark blue: used for chisels and large saws.

Allotropic forms of iron.—The changes occurring in the tempering of steels are believed to be the following. There are **three allotropic modifications of iron.** (1) **α-Ferrite** (the chief constituent of wrought-iron) is stable below 760°, is soft, magnetic, and capable of dissolving but little iron carbide, Fe_3C. (2) **β-Ferrite** is produced at 760°, it is non-magnetic, and dissolves only a little carbide. (3) **γ-Ferrite** is produced by heating to 900°; it is non-magnetic, but differs from the other two varieties in forming solid solutions with iron carbide. On cooling, the changes are reversed:

$$\alpha\text{-ferrite} \underset{760^\circ}{\rightleftharpoons} \beta\text{-ferrite} \underset{900^\circ}{\rightleftharpoons} \gamma\text{-ferrite}.$$

When fluid iron containing dissolved carbon is *quickly cooled* by quenching, it solidifies to γ-ferrite containing dissolved carbide, Fe_3C (**cementite**); the product, which is homogeneous, hard, and brittle, is known as **martensite** (hard steel).

When the cooling is carried out *slowly*, so that the mass passes through a succession of equilibrium states, solidification takes place at 1130°, with production of a heterogeneous mass of **martensite** (2 per cent. of C) and scales of **graphite.** As the temperature falls to 1000°, more graphite separates from the solid solution until the martensite contains 1·8 per cent. of dissolved carbon. At this point **cementite,** Fe_3C, begins to separate. At 670°, α-ferrite begins to separate, and the remaining solid solution then contains 0·9 per cent. of carbon. The solid solution will then slowly separate at this temperature into a heterogeneous mixture of 87 per cent. of soft α-ferrite and 13 per cent. of hard cementite, the mass, known as **pearlite,** thus containing the three phases: α-ferrite + cementite + graphite. The addition of manganese, nickel, etc., retards the conversion of γ-ferrite into α-ferrite and β-ferrite, and thus produces a more homogeneous steel, the Fe_3C remaining in solution as martensite.

These changes are attended with evolution of heat, which can be followed by observing the temperature of the cooling metal at various times by a pyrometer, and the separation of the various constituents may be observed by quenching, polishing the steel, etching the surface with reagents, and examining microscopically. The change taking place at about 760° is the cause of *recalescence*, the sudden re-heating of a mass of red-hot iron on cooling.

Wrought-iron is **case-hardened** by heating in contact with carbon or potassium ferrocyanide, when a surface-layer of steel is produced. **Armour-plate** is made by case-hardening a sheet of soft steel on one side and then spraying it with cold water. It is pierced in a clean hole by a soft-nosed shell, whereas hard steel splits in pieces. Nickel-chrome steels form very tough armour-plates.

Pure iron.—The soft iron wire used for binding flowers contains 99·7 per cent. of Fe; the perfectly pure metal is obtained by reducing pure ferric oxide in hydrogen, or by electrolysis of a solution of 1 part of ferrous chloride, 1 part of calcium chloride, and 1·6 parts of water at 110°. It is a soft, almost white, metal, sp. gr. 7·86, m.-pt. 1510°, b.-pt. 2450°. Iron is the most ductile and tenacious of all metals except nickel and cobalt. It is permeated by hydrogen at a red heat, and burns brilliantly in oxygen when heated to redness. Powdered iron prepared by reduction at a fairly low temperature is pyrophoric.

The rusting of iron.—Iron when exposed to ordinary moist air is quickly corroded to a reddish-brown **rust,** consisting chiefly of hydrated ferric oxide, $2Fe_2O_3.3H_2O$. The conditions under which rusting takes place have been investigated by several experimenters, with divergent results. The homogeneity or otherwise of the metal and its purity affect the results. The presence of water is essential, and according to some experimenters the presence of carbon dioxide is also necessary. Freshly-formed rust usually contains considerable quantities of ferrous hydroxide and carbonate, indicating that the formation of these compounds is probably the first step in the corrosion of the metal.

Crace Calvert (1876) and Crum Brown (1888) suggested the following reactions leading to the formation of rust :

1. $Fe + H_2O + CO_2 = FeCO_3 + H_2$.
2. $4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2$.

According to G. T. Moody (1906), pure iron does not rust in the presence of water and air if every trace of carbon dioxide is excluded. The iron first passes into solution, when carbon dioxide is present, as ferrous bicarbonate, $Fe(HCO_3)_2$, which then undergoes oxidation by dissolved oxygen, with precipitation of ferric hydroxide, according to the above equations. The addition of alkalies to the water, by diminishing the content of carbonic acid, retards the rusting of iron.

EXPT. 336.—Take four lots, (*a*), (*b*), (*c*), (*d*), of clean iron nails.

(*a*) Boil ordinary tap-water in a test-tube until it begins to " bump," showing that dissolved air has been expelled. Drop the nails (*a*) into the water, and boil again for half a minute. Pour melted vaseline over the surface of the water. This excludes air, so that iron and water alone are present.

(*b*) Place nails (*b*) in a test-tube full of ordinary water. In this case iron, much water, and air are present.

(*c*) Place nails (*c*) in a test-tube with a few drops of water. In this case iron, a little water, and air are present.

(*d*) Place nails (*d*) in a desiccator over sulphuric acid. In this case iron and air alone are present.

Leave the four specimens for a few days, and examine the iron. Rusting should have occurred only in cases (*b*) and (*c*).

EXPT. 337.—Pour 100 c.c. of 15 per cent. caustic potash solution into a 500 c.c. flask, fitted with a cork partly bored, and shake. Allow the flask to stand for two days. Boil a large bright nail with distilled water, as described above, and push it through the cork into the flask, leaving a short length outside. Allow to stand for a few days. The part of the nail inside the flask, which is exposed to air and water in the absence of carbon dioxide, does not rust, whilst the part outside, exposed to moisture and air containing carbon dioxide, will rust.

EXPT. 338.—It will be noticed in Expt. 336 (*b*) that the undersides of the nails remain bright, and rust is deposited on the top, exposed to air. This indicates that the iron passes into solution, and the solution is then oxidised by the air. Place a number of bright nails in a jar, cover them with a piece of hardened filter paper, and pour boiled distilled water into the jar. Rust is deposited *above* the filter-paper.

According to another theory of rusting, the different parts of a piece of iron act as poles of voltaic cells and solution of the metal occurs as the result of local action. This is quite compatible with the fact that oxidation occurs only in solution, since ferrous ions may be formed initially, but the action of carbonic acid is not introduced. Lambert (1912), who took the most rigid precautions to exclude carbon dioxide, found that, although homogeneous iron does not rust even in ordinary air, ordinary iron rusts in the absence of carbon dioxide.

EXPT. 339.—Prepare a solution of agar-agar in hot water (1½ per cent.), and add a little sodium chloride and phenolphthalein. Pour some of the solution over a clean plate of iron in a glass dish. The agar sets to a jelly. After some hours red patches appear, indicating the formation of caustic soda by electrolysis. If potassium ferricyanide and phenolphthalein are added to the agar, and the hot solution is poured over clean iron nails, the anodes become blue, from reaction of ferricyanide with ferrous ions, and the cathodes red, from the caustic potash formed.

The cause of rusting on this theory is electrolytic and due to the different solution pressures (p. 884) of different parts of the metal.

Iron is protected from rusting by painting, or whitewashing with lime. Pipes are also protected by heating and dipping into a solution of coal-tar pitch in coal-tar naphtha, when an impervious coating is formed (*Angus Smith's compound*). In the *Barff process*, the iron is heated to redness and steam blown over it, when an adherent layer of ferroso-ferric oxide is formed. This is used in treating cans for fruit, etc., instead of tinning. The layer of oxide is removed by heating with water containing magnesium chloride, which explains the corrosive action of sea-water on boilers.

Passive iron.—Iron is rendered passive (p. 949) by immersion in fuming nitric acid, chloric acid, chromic acid, or hydrogen peroxide, or by making it the anode in electrolysis. The metal is then insoluble in dilute acids, and does not precipitate copper from a solution of copper sulphate (Kier, 1790). The passivity is removed by touching with active iron under the surface of dilute sulphuric acid. The passivity may be due to a film of oxide, Fe_3O_4; it is removed by heating in hydrogen.

Salts and ions of iron.—Iron readily dissolves in dilute hydrochloric or sulphuric acids, producing **ferrous salts,** the solutions of which contain the bivalent **ferrous ion,** $Fe^{\cdot\cdot}$: $Fe + 2H^{\cdot} = Fe^{\cdot\cdot} + H_2$.

In dilute nitric acid, no gas is evolved, the acid is reduced, and ammonium nitrate formed:

$$8Fe + 20HNO_3 = 8Fe(NO_3)_2 + 2NH_4NO_3 + 6H_2O.$$

Solutions containing the ferrous ion are nearly colourless, but usually possess a green tinge, due apparently to the presence of traces of the ferric ion, $Fe^{\cdot\cdot\cdot}$. They have an inky taste, and readily undergo oxidation by atmospheric oxygen, insoluble basic ferric salts being deposited.

Ordinary **ink** contains ferrous sulphate, tannin (an organic substance obtained from gall-nuts or oak-bark), and gum. This solution, containing ferrous tannate, has a very pale colour, so that a solution of indigo-sulphuric acid, or a blue dye is added. On exposure to air, the ferrous tannate is oxidised to ferric tannate, which has an intense black colour, and the blue colour of the ink gradually changes to deep black.

The ferrous ion is readily converted by **oxidation** into the **ferric ion**, $Fe^{\cdot\cdot\cdot}$, which is also almost colourless, the red or brown colour of ordinary solutions of ferric salts being due to the undissociated compound, to basic compounds, or to colloidal ferric hydroxide formed by hydrolysis. If these brown solutions are mixed with concentrated nitric acid they become nearly colourless; with concentrated hydrochloric acid they become deep yellow, the colour of undissociated ferric chloride.

The oxidation of ferrous to ferric salts may be effected: (i) by atmospheric oxygen in neutral solutions, when insoluble basic ferric salts are precipitated; (ii) by chlorine or bromine: $2Fe^{\cdot\cdot} + Cl_2 = 2Fe^{\cdot\cdot\cdot} + 2Cl'$. The reaction with iodine is reversible: $2Fe^{\cdot\cdot} + I_2 \rightleftharpoons 2Fe^{\cdot\cdot\cdot} + 2I'$; ferric chloride liberates iodine from potassium iodide and iodine oxidises ferrous chloride to ferric chloride. Ferrous salts are also oxidised by boiling with nitric acid or *aqua regia*.

Ferric salts are reduced to ferrous salts by nascent hydrogen, in acid solution, say by a mixture of zinc and hydrochloric acid: $2Fe^{\cdot\cdot\cdot} + H_2 = 2Fe^{\cdot\cdot} + 2H^{\cdot}$.

A solution of silver nitrate oxidises a ferrous salt, silver being precipitated. In this case a transfer of ionic charge occurs: $Fe^{\cdot\cdot} + Ag^{\cdot} = Fe^{\cdot\cdot\cdot} + Ag$.

Oxides of iron.—Iron forms three well-defined **oxides**:

(1) **Ferrous oxide,** $\overset{II}{Fe}O$, a strong base, corresponding with the **ferrous salts,** *e.g.*, $\overset{II}{Fe}SO_4$ (which may be written on the old dualistic notation as FeO,SO_3); these are formed by dissolving iron in dilute acids.

(2) **Ferric oxide,** $\overset{III}{Fe}_2O_3$, a fairly strong base, corresponding with

the **ferric salts,** *e.g.*, $\overset{\text{III}}{Fe}_2(SO_4)_3$ ($Fe_2O_3,3SO_3$); with very strong bases unstable **ferrites,** *e.g.*, $Na_2\overset{\text{III}}{Fe}_2O_4$, are formed, so that ferric oxide has also feebly acidic properties.

(3) **Ferroso-ferric oxide,** Fe_3O_4, probably ferrous ferrite, $\overset{\text{II}}{Fe}(\overset{\text{III}}{Fe}O_2)_2$, or $\overset{\text{II}}{Fe}O,\overset{\text{III}}{Fe}_2O_3$.

(4) The unstable *ferrates*, *e.g.*, K_2FeO_4, correspond with an unknown acidic **trioxide,** FeO_3.

FERROUS SALTS.

Ferrous chloride, $FeCl_2$.—This salt is deposited from solutions of iron in hydrochloric acid in bluish-green monoclinic crystals, $FeCl_2,4H_2O$, which oxidise slightly, and become green in the air. The anhydrous chloride, $FeCl_2$, is obtained in white lustrous scales on heating iron in hydrogen chloride: $Fe + 2HCl = FeCl_2 + H_2$.

EXPT. 340.—Place a spiral of iron wire in a hard glass tube and pass over it dry hydrogen chloride. Heat the spiral strongly, and notice the sublimation of ferrous chloride. The escaping hydrogen may be ignited.

Anhydrous ferrous chloride volatilises at a bright red heat; its vapour density indicates that molecules of Fe_2Cl_4 and $FeCl_2$ are present. The density becomes normal between 1300° and 1500°: $Fe_2Cl_4 \rightleftharpoons 2FeCl_2$. On heating the substance in air, oxidation occurs; ferric chloride volatilises, and ferric oxide remains: $12FeCl_2 + 3O_2 = 2Fe_2O_3 + 8FeCl_3$. When ferrous chloride is heated in steam, hydrogen is evolved:

$$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2.$$

Ferrous bromide, $FeBr_2$, and **ferrous iodide,** FeI_2, are prepared similarly to the chloride, and form the crystalline hydrates $FeBr_2,6H_2O$ and $FeI_2,5H_2O$. They are also formed by adding the halogen to iron filings (in excess) in presence of water. If excess of iodine is used, **ferroso-ferric iodide,** Fe_3I_8, is formed, which gives with caustic potash a black precipitate of **ferroso-ferric hydroxide**: $Fe_3I_8 + 8KOH = Fe_3(OH)_8 + 8KI$. This reaction is used in the preparation of potassium iodide (p. 792).

Ferrous sulphate, $FeSO_4$.—This is the most important ferrous salt, and is obtained by dissolving iron in dilute sulphuric acid (p. 185), or by the slow oxidation of marcasite, or "coal-brasses," FeS_2, by air in presence of water. The common form is **green vitriol,** $FeSO_4,7H_2O$, crystallising in monoclinic crystals isomorphous with

Epsom salts, $MgSO_4,7H_2O$. If a crystal of *white vitriol*, $ZnSO_4,7H_2O$, is placed in the saturated solution *rhombic* crystals of $FeSO_4,7H_2O$, isomorphous with that salt, are deposited, whilst *blue vitriol*, $CuSO_4,5H_2O$, induces the deposition of *triclinic* isomorphous crystals of $FeSO_4,5H_2O$. By precipitating the solution with alcohol, or by heating green vitriol in a vacuum at 140°, the monohydrate, $FeSO_4,H_2O$, is formed, and this on heating at 300° in absence of air leaves the white, amorphous anhydrous salt, $FeSO_4$. Crystalline hydrates with 6, 3, and $2H_2O$ are also known.

Ferrous sulphate readily forms **double-salts** with the sulphates of the alkali-metals, $R_2SO_4,FeSO_4,6H_2O$. If equimolecular amounts of ferrous sulphate and ammonium sulphate are dissolved in separate amounts of hot water, and the filtered solutions mixed, **ferrous ammonium sulphate,** or **Mohr's salt,** $(NH_4)_2SO_4,FeSO_4,6H_2O$, is deposited on cooling in light bluish-green monoclinic crystals, which may also be deposited in the form of a practically white powder on adding alcohol to the solution (*cf.* $FeSO_4,7H_2O$). The crystals are stable in the air and the solution is much less readily oxidised by atmospheric oxygen than ferrous sulphate or chloride. Mohr's salt is therefore used in volumetric analysis for standardising solutions of potassium permanganate or dichromate; it contains almost exactly one-seventh of its weight of ferrous iron.

Ferrous carbonate, $FeCO_3$.—This compound occurs as *siderite*, or *spathic iron ore*, in rhombohedra isomorphous with calcite. It is formed as a white precipitate on addition of an alkali carbonate to ferrous salts. The precipitate rapidly becomes green, and finally brown, on exposure to air, owing to oxidation to ferric hydroxide. The addition of sugar retards the oxidation. Ferrous carbonate dissolves in water containing carbonic acid, forming **ferrous bicarbonate,** $Fe(HCO_3)_2$, which is sometimes present in rivers. On exposure to air, red ferric hydroxide is precipitated:

$$2Fe(HCO_3)_2 + O = Fe_2O_3 + 4CO_2 + 2H_2O.$$

Plants absorb iron from the soil as the bicarbonate.

Ferrous hydroxide, $Fe(OH)_2$.—This compound is thrown down as a white precipitate when caustic soda is added to a pure solution of a ferrous salt, with absolute exclusion of air. It is insoluble in excess of alkali, unless the latter is very concentrated, but dissolves slightly in ammonium salts. The precipitate rapidly becomes green in the air, from formation of $Fe_3(OH)_8$, and finally brown, forming $Fe(OH)_3$.

To obtain the original solution free from ferric salts, it is warmed with a little iron and dilute acid in a flask fitted with a tube dipping under water.

Ferrous oxide, FeO, is formed as a pyrophoric black powder by reducing ferric oxide with hydrogen at 300°, or by adding ferrous oxalate (obtained by precipitating ferrous sulphate with ammonium oxalate) to boiling caustic potash. It melts at 1420°. A mixture of FeO and finely-divided iron, which is pyrophoric, is obtained by heating ferrous oxalate at 150–160° in absence of air: $FeC_2O_4 = FeO + CO + CO_2$. Ferrous oxide is reduced to metallic iron by hydrogen at 700–800°.

Ferric Salts.

Ferric hydroxide, $Fe(OH)_3$.—If ammonium chloride and ammonia are added to a solution of a ferric salt, such as is obtained by oxidising ferrous sulphate with nitric acid or *aqua regia*, a reddish-brown, gelatinous precipitate of **ferric hydroxide,** $Fe(OH)_3$, is thrown down, which is slimy in the cold, but becomes flocculent on boiling. It is practically insoluble in water and alkalies, and is the form in which iron is separated in quantitative analysis. On prolonged boiling in contact with the solution, it becomes sparingly soluble in acids, whereas the freshly-formed precipitate is readily soluble. This appears to be due to loss of water. The precipitate is colloidal, and dries to a gum-like mass of indefinite composition. Crystalline hydrated ferric oxides occur in the minerals *limonite*, $2Fe_2O_3,3H_2O$, *göthite*, Fe_2O_3,H_2O, and *hydrohæmatite*, $2Fe_2O_3,H_2O$. On ignition, brownish-red **ferric oxide,** Fe_2O_3, is formed, which in this state is nearly insoluble in acids; it dissolves in concentrated hydrochloric acid only after digestion for several days, more easily in presence of ferrous salts. The best solvent is a boiling mixture of 8 parts of H_2SO_4 and 3 parts of water. If a current of hydrogen chloride is passed over the strongly-heated oxide, the latter becomes crystalline. Ferric oxide melts at 1563°. Red varieties of ferric oxide are formed by igniting ferrous sulphate in the air, and are used as paints or as a polishing powder (*rouge*, *crocus*, *colcothar*).

Colloidal ferric hydroxide is obtained by dissolving freshly-precipitated ferric hydroxide in a concentrated solution of ferric chloride, and dialysing. The blood-red solution (*dialysed iron*) is a positive colloid (p. 888), and is readily precipitated by salts. On adding concentrated hydrochloric acid, the solution is *slowly* converted into yellow ferric chloride. If glycerin, sugar, tartaric acid, etc., are added to a solution of a ferric salt, the latter is not precipitated by ammonia, but a clear brown colloidal solution is formed. If organic matter is present in a substance, it must therefore be destroyed by ignition before the ordinary group-reagents of qualitative analysis are used.

If ferric oxide is strongly heated with sodium carbonate, **sodium ferrite,** $Na_2Fe_2O_4$ (Na_2O,Fe_2O_3) is formed: $Na_2CO_3 + Fe_2O_3 = Na_2Fe_2O_4 + CO_2$. On treating the mass with hot water, the ferrite is decomposed and a solution of caustic soda is produced, the ferric oxide being regenerated: $Na_2Fe_2O_4 + H_2O = 2NaOH + Fe_2O_3$. This is the **Löwig process** for the manufacture of caustic soda.

Ferroso-ferric oxide, Fe_3O_4.—This oxide is strongly magnetic and is formed by heating iron to redness in air ("smithy scales"), or in steam. The pure oxide is obtained as a black powder by reducing Fe_2O_3 at 400° in a current of hydrogen and steam. It melts at 1540°, and is cast into electrodes, since it resists acids and chlorine when fused. **Ferroso-ferric hydroxide,** $Fe_3(OH)_8$, is formed as a black precipitate by adding caustic soda to a mixture of a ferrous and a ferric salt. It dissolves in hydrochloric acid to a green solution, from which crystals of **ferroso-ferric chloride,** $Fe_3Cl_8,18H_2O$, separate on evaporation. The oxide Fe_3O_4 appears to be ferrous ferrite, $Fe{:}(FeO_2)_2$.

Ferric chloride, $FeCl_3$.—This is the most important ferric salt. It is obtained anhydrous, in iron-black crystals with a green iridescence, on heating iron in chlorine (*cf.* Expt. 328). These volatilise on heating, and at 444° the vapour density corresponds with Fe_2Cl_6. With rise of temperature the vapour density falls, owing to dissociation, and at 750° becomes nearly equal to that required by the formula $FeCl_3$, although it still decreases, probably owing to dissociation into $FeCl_2$ and chlorine: $Fe_2Cl_6 \rightleftharpoons 2FeCl_3$; $2FeCl_3 \rightleftharpoons 2FeCl_2 + Cl_2$.

Temperature	448°	518°	606°	750°	1050°	1300°
$\triangle$ (H = 1) ..	151	138	121	78	76·3	73·4

In solutions in alcohol and ether the molecular weight of ferric chloride corresponds with $FeCl_3$. The anhydrous chloride is also soluble in benzene. These solutions exhibit the bright yellow colour of $FeCl_3$ molecules. Aqueous solutions containing excess of hydrochloric acid are also bright yellow. In alcoholic solution, containing water, ferric chloride is reduced on exposure to light, and green crystals of $FeCl_2,2H_2O$ are deposited.

Aqueous solutions of ferric chloride are produced by dissolving ferric hydroxide in hydrochloric acid, or by saturating solutions of ferrous chloride with chlorine. On evaporation, crystals containing $Fe_2Cl_6,12H_2O$, $Fe_2Cl_6,7H_2O$, $Fe_2Cl_6,5H_2O$, $Fe_2Cl_6,2H_2O$, and Fe_2Cl_6 are deposited at 37°, 32·5°, 56°, 73·5°, and (from solutions containing more ferric chloride than corresponds with $Fe_2Cl_6,2H_2O$) at 60°, respectively. If the solution is evaporated to the composition $FeCl_3,6H_2O$, yellow crystals are deposited on cooling, which are readily soluble in water. Ferric chloride solution is used as a styptic, *i.e.*, in stopping bleeding. It coagulates the blood, forming a clot. The solution is strongly acid, due to hydrolysis (p. 989): $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$. On heating the hydrated salts, hydrochloric acid is evolved, and a basic salt, or finally ferric oxide, is left.

Garnet-red **double salts** are formed from ferric chloride and other chlorides : $FeCl_3,2KCl,H_2O$, $FeCl_3,2NH_4Cl,H_2O$, $FeCl_3,MgCl_2,H_2O$.

Ferric fluoride, FeF_3, is a white, difficultly soluble salt, only slightly ionised in solution. It forms double fluorides, *e.g.*, Na_3FeF_6, analogous to cryolite (p. 898). The **bromide.** $FeBr_3$, is formed similarly to the chloride, but the iodide does not appear to exist (*cf.* p. 986).

Ferric phosphate, $FePO_4,2H_2O$, is obtained as a white precipitate, insoluble in acetic acid, but soluble in mineral acids, when sodium phosphate is added to a ferric salt. It is used in the separation of phosphates in qualitative analysis (p. 630).

Ferric sulphate, $Fe_2(SO_4)_3$.—A solution of this salt is obtained by boiling ferrous sulphate with sulphuric and nitric acids. Nearly pure nitric oxide is evolved : $6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_2 + 2NO + 4H_2O$. A black solution containing $FeSO_4 \cdot NO$ (p. 580) is first formed. A similar reaction occurs with ferrous chloride and *aqua regia*, ferric chloride being produced. The reaction is used in the estimation of nitrates (Schloesing) ; the nitric oxide evolved is measured. Prolonged boiling, preferably under reduced pressure, is, however, necessary to complete the reaction.

Ferric sulphate is also formed by evaporating ferrous sulphate with concentrated sulphuric acid :

$$2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 2H_2O.$$

Anhydrous ferric sulphate is a yellowish-white powder, dissolving only very slowly in water, but ultimately forming a very concentrated solution. This is slightly yellow owing to hydrolysis, but becomes nearly colourless on addition of sulphuric acid. With potassium and ammonium sulphates ferric sulphate forms **iron alums,** *e.g.*, $(NH_4)_2SO_4,\overset{\text{III}}{Fe_2}(SO_4)_3,24H_2O$, with a slight yellow tinge when pure, but often violet, possibly owing to the presence of manganese. These are readily soluble in water, and are not appreciably hydrolysed. The potassium alum, $K_2SO_4,Fe_2(SO_4)_3,24H_2O$, does not crystallise so readily as the ammonium salt.

On heating ferric sulphate, sulphur trioxide is evolved, the reaction being reversible : $Fe_2(SO_4)_3 \rightleftharpoons Fe_2O_3 + 3SO_3$.

Ferric nitrate is obtained by dissolving iron in fairly concentrated nitric acid ; the dark brown solution (used as a mordant) deposits colourless cubic [$Fe(NO_3)_3,6H_2O$] or monoclinic [$Fe(NO_3)_3,9H_2O$] crystals.

If iron is dissolved in sulphurous acid no gas is evolved. The solution deposits colourless crystals of **ferrous sulphite,** and a solution of **ferrous thiosulphate** is left : $2Fe + 3H_2SO_3 = FeSO_3 + FeS_2O_3 + 3H_2O$.

Iron salts act as **catalysts** in many reactions. Thus, if hydrogen peroxide is added to potassium iodide and starch acidified with acetic acid, iodine is only slowly liberated, but on addition of a drop of ferrous sulphate the reaction is instantaneous. The iron in chlorophyll and hæmoglobin may have something to do with the activity of these substances.

Iron carbonyls.—When carbon monoxide is passed over finely divided iron at 120°, **iron pentacarbonyl,** $Fe(CO)_5$, is produced. It is a pale yellow, viscous liquid, b.-pt. 102·5°, fr.-pt. —20°. The vapour is decomposed on passage through a tube heated to 180°, a mirror of metallic iron being deposited. The vapour density at 129°, and the freezing point of the solution in benzene, correspond with the above formula. Iron pentacarbonyl is decomposed by air and moisture, and by acids : $Fe(CO)_5 + H_2SO_4 = FeSO_4 + 5CO + H_2$. On exposure to light, **diferro-nonacarbonyl** is formed, the reaction being reversed in darkness : $2Fe(CO)_5 \rightleftharpoons Fe_2(CO)_9 + CO$. $Fe_2(CO)_9$ forms orange crystals, decomposing on heating : $Fe_2(CO)_9 = Fe(CO)_5 + Fe + 4CO$. If a solution of $Fe_2(CO)_9$ in toluene is heated to 50° it becomes intensely green, and green crystals are deposited, which are a polymerised form of **iron tetracarbonyl,** $Fe(CO)_4$.

Iron pentacarbonyl is formed in traces when water-gas (p. 705) is passed through iron pipes. Such gas deposits Fe_2O_3 on incandescent mantles in gas-burners.

Sulphides of iron.—**Ferrous sulphide,** FeS, is formed as a black mass by heating iron filings together with sulphur, a considerable amount of heat being evolved. It may be prepared by dipping a white-hot bar of wrought-iron into molten sulphur in a crucible. (Cast-iron is not attacked.) A mixture of iron filings and sulphur when moistened becomes heated and forms FeS. Ferrous sulphide in the pure state is a yellowish, crystalline mass with a metallic lustre, melting at 1300°. The commercial substance is black or dark-grey, and contains free iron. It dissolves readily in dilute acids, and is used in the preparation of sulphuretted hydrogen (p. 483). A greenish-black precipitate of ferrous sulphide is formed when ammonium sulphide is added to a ferrous salt : $(NH_4)_2S + FeSO_4 = FeS + (NH_4)_2SO_4$. The precipitate dissolves slightly in excess of the reagent when the latter contains polysulphides, forming a dark greenish - black solution, probably containing a **ferri - sulphide,** $(NH_4)FeS_2$, or $(NH_4)_2S,Fe_2S_3$.

Potassium ferri-sulphide, $KFeS_2$, is formed in purple crystals by fusing together iron, sulphur, and potassium carbonate, and extracting with water. On heating in hydrogen it forms a **ferrosulphide,** $K_2Fe_2S_3$, or $K_2S,2FeS$. The sodium salt, $NaFeS_2,4H_2O$, occurs in the crude black liquors obtained by lixiviating black-ash (p. 778). It is removed, and the soda liquor decolorised, by heating with zinc oxide, when Fe_2O_3 is precipitated, and white ZnS formed.

Iron sesquisulphide, Fe_2S_3, is formed as a yellow mass with metallic lustre, by heating FeS with sulphur, or by heating iron powder in H_2S at 100° ; it is thrown down as a black precipitate by the action of excess of ammonia and ammonium sulphide on a solution of a ferric salt ; with excess of ferric salt a mixture of 2FeS and S is formed. The mineral *magnetic pyrites* consists of compounds of FeS and Fe_2S_3 varying from $5FeS,Fe_2S_3$ to $6FeS,Fe_2S_3$. **Tetraferric trisulphide,** Fe_4S_3, is said to be formed by heating iron in carbon disulphide vapour.

Iron disulphide, FeS_2, occurs as *iron pyrites* and *marcasite*. *Pyrites* (sp. gr. 5·19) is stable in air, marcasite (sp. gr. 4·68–4·85) oxidises in moist air to ferrous sulphate. **Pyrites** crystallises in the regular system, often in cubes, either plain or striated ; sixty-nine forms have been described. It has a brassy-yellow colour (" fools' gold "), is very hard, striking sparks from steel, and is not magnetic. **Marcasite** occurs in rhombic crystals, usually in the form of radiating nodules, and is white like tin. Pyrites often occurs in coal and is the main source of the sulphur dioxide formed on its combustion. It is found in masses having the form of wood, roots, etc., and has probably been formed by the reduction of solutions of ferrous sulphate by organic matter. Pyrites is insoluble in dilute acids but dissolves readily in concentrated nitric acid, with separation of sulphur, or in *aqua regia*.

Ferric acid.—A mixture of one part of iron filings and two parts of nitre deflagrates on heating, and the cold product dissolves in water to form a purple solution (Stahl, 1702). This contains the potassium salt of **ferric acid,** H_2FeO_4 (Fremy, 1841). The purple solution is also produced by the electrolysis of caustic potash with a cast-iron anode, or by passing chlorine through ferric hydroxide suspended in potash. If excess of caustic potash is added, reddish-brown **potassium ferrate,** K_2FeO_4, is deposited. On boiling, a yellow solution of **potassium ferrite,** $K_2Fe_2O_4$, is produced, which rapidly deposits ferric hydroxide. On addition of barium chloride to the red potassium ferrate solution, fairly stable **barium ferrate,** $BaFeO_4,H_2O$, is formed as a red precipitate.

Potassium ferrocyanide, $K_4Fe(CN)_6$.—No simple cyanides of iron are known ; if potassium cyanide is added to a solution of ferric chloride, cyanogen is evolved, and ferric hydroxide is precipitated : $2FeCl_3 + 6KCN + 6H_2O = 2Fe(OH)_3 + 6HCN + 6KCl$. Many **complex cyanides,** however, are known. When nitrogenous organic matter, such as horn or leather-clippings, is fused with potassium carbonate and iron filings and the mass digested with water, the solution deposits on evaporation yellow crystals of **potassium ferrocyanide,** or **yellow prussiate of potash,** $K_4Fe(CN)_6,3H_2O$. The addition of a ferric salt to the solution gives a deep blue precipitate of **Prussian blue,** the first ferrocyanogen compound to be discovered (Diesbach, 1704). Macquer (1752) showed that potassium ferrocyanide was formed on boiling Prussian blue with potash, and Porret (1814) observed that the former salt contained a peculiar acid, **ferrocyanic acid,** $H_4Fe(CN)_6$, formed as a white precipitate on adding an acid, and then ether, to a solution of the ferrocyanide. The precipitate contains combined ether. Berzelius pointed out that the yellow prussiate might be regarded as a double cyanide of potassium and iron, $4KCN,Fe(CN)_2$, but since it shows none of the reactions of iron or of cyanides, it is more properly regarded as the potassium salt of the complex ferrocyanic acid: $K_4[Fe(CN)_6]$. One of the CN groups may be replaced by CO, H_2O, NO, NO_2, etc.

Potassium ferrocyanide is often prepared from the spent-oxide of gas works (p. 682) by boiling with potash and crystallising. The nitrogen of the coal is partly evolved as cyanogen, which collects in the oxide purifiers in the form of Prussian blue. The salt is also formed by adding excess of potassium cyanide to a solution of ferrous sulphate, until the brown precipitate redissolves. The crystals are yellow, tetragonal pyramids, which are unchanged in air but on heating fall to a white powder of anhydrous salt. Potassium ferrocyanide is not poisonous. The sodium salt, $Na_4Fe(CN)_6,10H_2O$, is prepared in a similar manner. Silver nitrate gives a white precipitate of silver ferrocyanide, $Ag_4Fe(CN)_6$, with soluble ferrocyanides.

Potassium ferricyanide, $K_3Fe(CN)_6$.—If chlorine is passed through a solution of potassium ferrocyanide, the quadrivalent **ferrocyanide ion,** $\overset{II}{Fe}(CN)_4''''$, is *oxidised* (p. 255) to the tervalent **ferricyanide ion,** $\overset{III}{Fe}(CN)_6'''$, the two ions containing bi- and ter-valent iron respectively: $2Fe(CN)_6'''' + Cl_2 = 2Fe(CN)_6''' + 2Cl'$. At the same time a molecule of chlorine gas is *reduced* to two chloride ions. The two salts KCl and $K_3Fe(CN)_6$ separate on evaporation from the yellowish-brown solution, but by repeated recrystallisation **potassium ferricyanide,** $K_3Fe(CN)_6$, is obtained in the pure state in the form of anhydrous dark-red monoclinic prisms (*red prussiate of potash,* L. Gmelin, 1822). It is an oxidising agent, converting litharge into lead dioxide, and chromium sesquioxide into potassium chromate, when these are boiled with the alkaline solution: $6K_3Fe(CN)_6 + Cr_2O_3 + 10KOH = 6K_4Fe(CN)_6 + 2K_2CrO_4 + 5H_2O$ (or $4Fe(CN)_6'''2 + Cr^{\cdot\cdot} + 10OH' = 4Fe(CN)_6'''' + 2CrO_4'' + 5H_2O$). It is used in organic chemistry for effecting oxidations. The solution is reduced by sodium amalgam and by glucose in alkaline solution to ferrocyanide. The alkaline solution is reduced by hydrogen peroxide, whereas an acid solution of ferrocyanide is oxidised by the same reagent (p. 340). **Sodium ferricyanide,** $2Na_3Fe(CN)_6,H_2O$, is obtained from sodium ferrocyanide and chlorine.

Ferricyanic acid, $H_3Fe(CN)_6$, is formed in brown needles by decomposing lead ferricyanide [obtained in brown crystals, $Pb_3(FeCy_6)_2,16H_2O$, by mixing hot solutions of $Pb(NO_3)_2$ and $K_3Fe(CN)_6$] with sulphuric acid and evaporating. Silver salts give a red precipitate of **silver ferricyanide,** Ag_3FeCy_6, with ferricyanides.

Prussian blue.—When a solution of ferrous sulphate is added to a cold *neutral* solution of potassium ferrocyanide, a white precipitate of **potassium ferrous ferrocyanide,** $K_2\overset{II}{Fe}(\overset{II}{Fe}Cy_6)$, is formed, which rapidly oxidises in air to **β-soluble Prussian blue,** or potassium ferric ferrocyanide, $\overset{III}{Fe}K(\overset{II}{Fe}Cy_6),H_2O$, insoluble in oxalic acid but soluble in water. But if ferrous sulphate is added to an *acid* solution of ferrocyanide the white precipitate formed, although similar to the above, is less readily oxidised, and on exposure to air forms **γ-soluble Prussian blue,** probably of the same formula as the β-blue, but more stable to alkalies, acids, and ferric chloride.

When potassium ferrocyanide is boiled with dilute sulphuric acid, hydrocyanic acid (p. 717) is evolved, and may be obtained in the form of a dilute solution by attaching a Liebig's condenser to the flask: $2K_4FeCy_6 + 3H_2SO_4 = 3K_2SO_4 + K_2\overset{II}{Fe}(\overset{II}{Fe}Cy_6) + 6HCN$. The pale yellow powder, $K_2\overset{II}{Fe}(\overset{II}{Fe}Cy_6)$, left in the flask is much less easily oxidised than the other two forms just described, but nitric acid or hydrogen peroxide converts it into **Williamson's violet,** $K\overset{III}{Fe}(\overset{II}{Fe}Cy_6),H_2O$.

By heating a solution of ferrocyanic acid at 110–120° in a sealed tube a precipitate of the acid corresponding with the white precipitates, ferrous hydrogen ferrocyanide, $H_2\overset{II}{Fe}(\overset{II}{Fe}Cy_6)$, is formed, which on oxidation gives a violet compound, possibly $H\overset{III}{Fe}(\overset{II}{Fe}Cy_6)$.

When a solution of potassium ferrocyanide is precipitated with rather less than the equivalent of ferric chloride, and the precipitate washed by decantation with potassium chloride solution, it forms **α-soluble Prussian blue,** or **α-ferric ferrocyanide,** $4\overset{III}{Fe}K(\overset{II}{Fe}Cy_6),7H_2O$. This, when dried, has a bronze lustre and forms a beautiful deep blue powder. It dissolves in water, forming a blue colloidal solution, and is soluble in oxalic acid.

Prussian blue may, of course, have the possible formulæ: $\overset{III}{Fe}K(\overset{II}{Fe}Cy_6)$ or $\overset{II}{Fe}K(\overset{III}{Fe}Cy_6)$. K. A. Hofmann (1904) showed that hydrogen peroxide in acid solution, which reduces ferricyanides to ferrocyanides, oxidises ferrous ferrocyanides to Prussian blue; the latter must therefore contain the ferric iron in the basic radical. The same Prussian blue is formed by precipitating a ferricyanide with a ferrous salt; in this case isomeric change must have occurred.

With excess of ferric chloride, the precipitate becomes insoluble in water, and is called **insoluble Prussian blue**; it has the formula $\overset{III}{Fe}_4(\overset{II}{Fe}Cy_6)_3$, but contains water which cannot be driven off by heat. It is the ordinary Prussian blue of commerce.

The precipitate obtained by adding an excess of ferrous salt to potassium ferricyanide, known as **Turnbull's blue**, was formerly considered to be ferrous ferricyanide, $\overset{II}{Fe}_3(\overset{III}{Fe}Cy_6)_2$; it is, however, identical with insoluble Prussian blue. A ferric salt with potassium ferricyanide gives a deep brown solution, probably containing ferric ferricyanide, but no precipitate. A little stannous chloride, or granulated zinc and acid, added to the solution, precipitates Prussian blue. If chlorine is passed through a *boiling* solution of potassium ferrocyanide in the dark, a green precipitate of **ferric ferricyanide,** probably polymerised, $\overset{III}{Fe}(\overset{III}{Fe}Cy_6)$, is formed.

Sodium nitroprusside.—When potassium ferrocyanide is warmed with 50 per cent. nitric acid, a brown solution is produced. When the reaction has proceeded to such a stage that a slate-coloured precipitate is formed with ferrous sulphate the liquid is cooled, separated from the crystals of potassium nitrate, and neutralised with sodium carbonate. The filtered solution on evaporation gives red crystals, which may be freed from nitrate by repeated crystallisation, and consist of **sodium nitroprusside,** or **sodium nitrosoferricyanide,** $Na_2\overset{III}{Fe}(NO)Cy_5,2H_2O$. It is used as a reagent, giving an intense purple colour, due to the formation of $Na_3\overset{III}{Fe}(O{:}N{\cdot}SNa)Cy_5$, with alkali-sulphides, but not with free sulphuretted hydrogen. With silver nitrate a solution of a nitroprusside (which soon decomposes, and is made as required) gives a flesh-coloured precipitate of the silver salt. By decomposing this with hydrochloric acid, unstable free **nitrosoferricyanic acid**, $H_2Fe(NO)Cy_5$, is formed. This is also formed by passing nitric oxide into an acidified solution of potassium ferrocyanide.

Ferric thiocyanate, $Fe(CNS)_3$.—This salt is formed when potassium or ammonium thiocyanate is added to a solution of a ferric salt. It has a deep blood-red colour, and its formation is a delicate test for the ferric ion. The reaction is reversible (p. 350): $FeCl_3 + 3KCNS \rightleftharpoons Fe(CNS)_3 + 3KCl$. If the solution is shaken with ether, the latter dissolves the ferric thiocyanate, leaving the aqueous layer colourless. Mercuric chloride discharges the red colour of the aqueous solution; the mercury salt, which is only slightly ionised, is formed from the ferric salt. Reducing agents form ferrous thiocyanate, also colourless in solution. The red colour of the ferric salt is due to the undissociated molecules.

Peculiar series of complex iron compounds, containing nitrogen and sulphur, are known. If a solution of ferrous sulphate in excess of a thiosulphate is saturated with nitric oxide, crystalline **iron dinitrosothiosulphates** are formed, *e.g.*, reddish-brown leaflets of $K[Fe(NO)_2S_2O_3],H_2O$; brilliant jet-black crystals of $Rb[Fe(NO)_2S_2O_3],H_2O$. If nitric oxide is passed through a suspension of precipitated ferrous sulphide in dilute solutions of sulphides, black compounds (**Roussin's salts**) are formed, *e.g.*, $KFe_4(NO)_7S_3$, which form dark brown solutions with water. By the action of alkalies on these, salts such as $K_2Fe_2(NO)_4S_2$ are formed.

EXERCISES ON CHAPTER XLVIII

1. Discuss the position of the transitional elements in the Periodic System. What other elements show analogies to them?
2. What are the important ores of iron? How is cast-iron obtained from the ores?
3. How are steel and malleable iron produced from cast-iron? What is the cause of the different properties of these varieties of iron?
4. Describe briefly the changes occurring in the hardening and tempering of steel. What special varieties of steel are made?
5. How are the oxides of iron prepared? Discuss their properties with special reference to their acidic and basic character.
6. How are ferrous and ferric chlorides prepared? In what way can ferrous chloride be converted into ferric chloride, and *vice versa*?
7. Describe the preparation and properties of ferrous and ferric sulphates. What important double salts of these compounds exist? How would you prepare them from metallic iron?
8. How are iron carbonyls prepared?
9. Describe the preparation of (*a*) potassium ferrocyanide, (*b*) potassium ferricyanide, (*c*) sodium nitroprusside.
10. Give a brief account of the cyanogen compounds of iron.

CHAPTER XLIX

COBALT AND NICKEL

COBALT. $Co = 58{\cdot}50$.

Cobalt.—The copper-miners of the Hartz Mountains frequently obtained ores looking like copper-ore: these gave an unpleasant smell of garlic on roasting, and furnished no copper. The miners attributed their occurrence to the pranks of an evil spirit, *kobold*, and the material was called "false-ore," or *cobalt*.

In the mines of Chemnitz, the Baroness de Beausoleil claimed to have seen "aged dwarfs, three or four hands in height, clothed like miners in an old robe, with a leather apron hanging from the waist, a white coat, and a cowl. They carried lamps and picks, and were terrifying apparitions to those who had not the assurance gained by experience in the mines."

The residue left after roasting cobalt, called *zaffre* (impure cobalt arsenate), was found to give on fusion with sand and potassium carbonate a beautiful blue glass, called *smalt*. The despised ore began to be valued, and the work of the "evil spirit of the mine" beautified the magnificent stained glass windows of the churches. The blue colour, believed to be due to arsenic, was shown by Brandt (1735) to originate from a new metal contained in the ore, which he called *cobalt rex*: Bergman (1780) investigated its properties, and the metal then became known simply as **cobalt**. The "false-ore" is an arsenide of cobalt, iron, and nickel, $(Fe,Ni,Co)As_2$ (in the pure state, $CoAs_2$), it is known as *speiss cobalt*, or *smaltite*. A similar ore is *linnœite*, $(Co,Ni,Fe)_3S_4$. Cobalt is also found as *cobalt glance*, or *cobaltite*, $(Co,Fe)SAs$, and as *cobalt bloom*, $Co_3(AsO_4)_2,8H_2O$, but is now mainly obtained from the silver ores of Cobalt City, Ontario, and of New Caledonia, where arsenides of nickel and cobalt occur plentifully.

Metallurgy of cobalt.—The ore is roasted to free it from arsenic and sulphur, and fused in a blast-furnace with limestone and sand as a flux. The iron passes into the slag, and impure oxide of cobalt (*speiss*) settles out. This is extracted with hydrochloric acid, metals of the second group precipitated with sulphuretted hydrogen, and from the filtrate, boiled with bleaching powder to oxidise the iron, the latter is thrown down by milk of lime. The filtrate contains cobalt and nickel salts, and excess of lime; if a further addition of bleaching powder is made the cobalt is precipitated as a black **peroxide,** Co_2O_3 (p. 162), which is reduced by heating in hydrogen. Nickel is precipitated from the filtrate by adding excess of milk of lime. The Canadian ores are roasted, or leached with ferrous sulphate solution, when sulphates are formed. These are soluble and the cobalt is precipitated as before. The metal may also be precipitated by potassium nitrite as **potassium cobaltinitrite,** $K_3Co(NO_2)_6$. The **metal** is prepared by the electrolysis of a solution of the sulphate, $CoSO_4$, containing ammonium sulphate and ammonia. It is tenacious, silver-white in colour, with a slight pink tinge, readily polished, and shows a high lustre. Its specific gravity is 8·8, it is magnetic up to 1150°, and melts at 1530°. Cobalt slowly oxidises on heating in air. It absorbs 59–153 volumes of hydrogen when in a finely-divided state. The metal dissolves slowly in dilute sulphuric and hydrochloric acids, and readily in nitric acid. It can become passive in nitric acid.

Cobalt oxides.—The solution of cobalt in nitric acid contains **cobalt nitrate,** $Co(NO_3)_2,6H_2O$, which may be obtained on evaporation in pink crystals, which lose water over sulphuric acid to form a pink powder. This readily decomposes on heating, leaving black **cobalto-cobaltic oxide,** Co_3O_4. The solutions of cobalt salts are pink, and contain the bivalent **cobalt ion,** $Co^{\cdot\cdot}$. On addition of caustic potash, a bluish-violet precipitate of a basic salt is thrown down, which on boiling is converted into pink **cobaltous hydroxide,** $Co(OH)_2$. When heated out of contact with air, this forms an olive-green powder of the basic **cobaltous oxide,** CoO. Cobaltous hydroxide dissolves only in traces in excess of caustic potash, but is readily soluble in ammonia, a yellowish-brown solution of a complex compound being formed. This deposits cobaltous hydroxide on dilution, but readily absorbs oxygen from the air to form stable complex compounds known as *cobaltammines* (p. 1001).

On gently igniting cobalt nitrate, a **sesquioxide,** Co_2O_3, is obtained as a dark brown powder. This is probably the oxide formed when bleaching-powder, or iodine and caustic potash, is added to a solution of a cobaltous salt, although this may be CoO_2.

When hydrogen peroxide is added to cobaltous hydroxide suspended in water, the filtrate is acid, and becomes green on addition of potassium hydrogen carbonate. **Cobaltic acid,** H_2CoO_3, or a complex cobalt compound, $[\overset{III}{Co}(KCO_3)_2]_2O$, may be formed.

Both CoO and Co_2O_3 on ignition in air form Co_3O_4, and when heated in hydrogen all the oxides are reduced to the metal.

A solution of cobalt nitrate is used in blowpipe analysis for the detection of zinc and aluminium compounds. The ignited residue on charcoal is moistened with one drop of dilute cobalt nitrate and reheated. Zinc gives a *green* mass (Rinman's green, cobalt zincate, $CoZnO_2$); aluminium a *blue* mass [Thenard's blue, cobalt aluminate, $Co(AlO_2)_2$], although blue masses are also produced with phosphates. Magnesia gives a pink mass. Cobalt salts give a beautiful dark blue borax bead.

Cobalt salts.—With the exception of the blue **cobaltic sulphate,** $Co_2(SO)_3,18H_2O$, which forms alums, and is obtained by the electrolytic oxidation of cobaltous sulphate; and the dark brown unstable solutions of Co_2O_3 in acids, which contain the tervalent **cobaltic ion,** $Co^{\cdot\cdot\cdot}$, all the simple cobalt salts are derived from bivalent cobalt. The complex cobaltammines contain tervalent cobalt.

Cobaltous chloride, $CoCl_2,6H_2O$, is obtained in dark-red, deliquescent crystals from a solution of cobalt or the oxide in hydrochloric acid. It forms a number of lower hydrates. The anhydrous salt (and the lowest hydrates), obtained by heating, are deep blue in colour. A solution of cobalt chloride is used as a *sympathetic ink*; the writing is almost invisible, but becomes blue on holding the paper before the fire. On standing in moist air, the colour again disappears.

Other sympathetic inks, which are "irreversible," are dilute sulphuric acid, which chars the paper on heating, and a lead or bismuth salt, which becomes black on exposure to sulphuretted hydrogen. The latter is the original invisible ink (N. Lemery, 1681). The cobalt ink was introduced in 1705.

The pink solutions of cobalt chloride also become blue on heating, or addition of hydrochloric acid, or alcohol. A complex blue anion, $CoCl_4''$, appears to be formed: $2CoCl_2 \rightleftharpoons Co^{\cdot\cdot} + CoCl_4''$, which moves to the anode in electrolysis.

Cobaltous sulphate, $CoSO_4,7H_2O$, is isomorphous with the vitriols (*e.g.*, $FeSO_4,7H_2O$). It crystallises with different amounts of water, according to the temperature; the solution at 40–50° deposits $CoSO_4,6H_2O$, and when poured into concentrated sulphuric acid, $CoSO_4,4H_2O$. The anhydrous salt is pink. Double sulphates, *e.g.*, $K_2SO_4,CoSO_4,6H_2O$, are known.

Cobalt sulphide, CoS, is precipitated by ammonium sulphide, or by sulphuretted hydrogen in presence of sodium acetate. It is black, and, although not precipitated by sulphuretted hydrogen from acid solutions, it is insoluble in dilute acids; it is soluble in *aqua regia*.

By heating CoS with sulphur in a current of hydrogen, CoS_2, Co_2S_3, and Co_2S are said to be formed. A **persulphide,** possibly Co_2S_7, is formed as a black precipitate with yellow ammonium sulphide. **Cobaltous carbonate,** $CoCO_3$, forms a bright red precipitate. **Cobalt carbonyl,** $Co_2(CO)_8$, is obtained in orange-red crystals, m.-pt. 51°, by heating cobalt at 150° in carbon monoxide under 30 atm. pressure. At 60°, it forms $Co(CO)_3$, giving black crystals from a solution in benzene. The **carbide,** Co_3C, formed at high temperatures, is almost completely decomposed on cooling.

Blue cobalt glass, and the blue glazes on porcelain contain the **orthosilicate,** Co_2SiO_4. If stannic oxide is added, the **orthostannate,** Co_2SnO_4, is formed.

Complex cobalt compounds.—When potassium cyanide is added to a solution of a cobalt salt, a brownish-white precipitate of **cobaltous cyanide,** $Co(CN)_2$, is thrown down. This dissolves in excess of cyanide, forming **potassium cobaltocyanide,** $K_4\overset{II}{Co}(CN)_6$, analogous to the ferrocyanide, which is thrown down as a deep amethyst-coloured powder by alcohol. If a little acetic or hydrochloric acid is added to the solution, and the latter boiled in an evaporating dish for a few minutes, oxidation occurs and **potassium cobalticyanide,** $K_3\overset{III}{Co}(CN)_6$, analogous to the ferricyanide, is formed: $2K_4Co(CN)_6 + H_2O + O = 2K_3Co(CN)_6 + 2KOH$. An equivalent amount of hydrogen peroxide is contained in solution, so that **autoxidation** probably occurs: $H_2O + O_2 = H_2O_2 + O$. The cobalticyanide forms stable, yellow crystals, isomorphous with $K_3Fe(CN)_6$. It gives a blue precipitate with copper sulphate, $Cu_3(CoCy_6)_2$, and a white precipitate with silver nitrate, from which crystalline **cobalticyanic acid,** H_3CoCy_6, is formed with H_2S. Cobalticyanides give none of the reactions of cyanides or of cobalt, and are not decomposed by concentrated nitric acid.

Potassium nitrite gives with a solution of cobaltous sulphate acidified with acetic acid a yellow precipitate of **potassium cobaltinitrite,** $K_3Co(NO_2)_6$, which is slightly soluble in water. The precipitate may be washed with potassium acetate solution and alcohol. Potassium cobaltinitrite is decomposed by ammonium sulphide. The cobaltinitrite is produced only in acidified solutions; if acetic acid is not added, a double salt, $Co(NO_2)_2,2KNO_2$, is formed.

A reagent for potassium salts is prepared by dissolving 30 gm. of cobalt nitrate and 50 gm. of sodium nitrite in 150 c.c. of water and adding 10 c.c. of glacial acetic acid. The salts $K_2Ag[Co(NO_2)_6]$ and $KAg_2[Co(NO_2)_6]$ are less soluble than $K_2[Co(NO_2)_6]$, hence the addition of silver nitrate to the above reagent renders it still more sensitive; 1 part of potassium in 10,000 parts of water may be detected by the sodium silver cobaltinitrite reagent.

On addition of excess of ammonia to a cobalt salt, a clear solution is formed which absorbs oxygen from the air, forming complex compounds known as **cobaltammines,** which contain ammonia united with a cobaltic compound, *e.g.*, $[Co(NH_3)_6]Cl_3$. These show none of the reactions of cobalt; the metal is present in the form of complex radicals, *e.g.*, $Co(NH_3)_6$. The structure of the cobaltammines will be considered in connection with Werner's theory of valency (p. 1010).

NICKEL. Ni = 58·21.

Nickel.—The old German miners of Westphalia frequently obtained a mineral resembling copper ore, from which, however, no metal could be extracted, and to this the name *kupfer-nickel* (*i.e.*, "false-copper," Hiarni, 1694) was applied in derision. In 1750, Cronstadt obtained impure metallic nickel from this ore, the properties of the element being investigated more thoroughly by Bergman in 1774.

The chief **ores of nickel** are the cobalt ore *smaltite*, $(Ni,Co,Fe)As_2$; *white nickel ore*, $NiAs_2$; *kupfer-nickel*, or *niccolite*, NiAs; *nickel glance*, NiAsS; *millerite*, NiS; and the important ores, *garnierite*, a double silicate of nickel and magnesium, $2(Ni,Mg)_5Si_4O_{13},3H_2O$, found in New Caledonia, and *pentlandite*, $(Ni,Cu,Fe)S_2$, containing about 2·5 per cent. of nickel, found at Sudbury, Ontaria. *Nickel ochre*, $Ni_3(AsO_4)_2,8H_2O$, also occurs, and the magnetic pyrites of Pennsylvania contain about 5 per cent. of nickel.

Metallurgy of nickel.—The Sudbury ores, and garnierite, are roasted, smelted, and bessemerised, yielding **monel metal,** containing 67 per cent. of Ni, 28 of Cu, and 5 of Mn and Fe, used for sheet metal work. If monel metal is melted with coke and salt-cake (which form sodium sulphide) in a basic-hearth furnace, and poled, two strata separate. The upper layer contains sodium sulphide and cuprous sulphide, the lower layer is nickel sulphide, NiS. This is roasted to nickel oxide, NiO, and the latter reduced by heating strongly with charcoal powder.

Large quantities of nickel are extracted from the Canadian ores by the **Mond carbonyl process,** worked at Clydach in South Wales. In this process (Ludwig Mond, 1895), the roasted ore is leached with dilute sulphuric acid to remove copper, which is converted into blue vitriol. The residue is reduced at a temperature below 400° by the hydrogen contained in water gas. The ferric oxide is not reduced at this temperature, but nickel oxide forms metallic nickel. The mass is next passed down a tower provided with shelves, which is heated at 80°, and carbon monoxide passed through, when volatile **nickel carbonyl,** $Ni(CO)_4$, is produced. This is passed through tubes heated at 180°. Decomposition occurs, and metallic nickel is deposited: $Ni(CO)_4 \rightleftharpoons Ni + 4CO$, the carbon monoxide passing back to the volatiliser.

The carbon monoxide is prepared by absorbing carbon dioxide from flue-gas in a solution of potassium carbonate, heating the bicarbonate to drive off pure carbon dioxide, and passing the latter over incandescent coke.

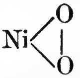
The total production of nickel in 1909 was about 16,000 tons, 2800 of which were obtained in England by the Mond Nickel Co.

The metal may be cast. A little magnesium is usually added before casting, to increase the fluidity and to remove gas-bubbes.

Nickel is **refined** by electrolytic deposition from a solution of nickel ammonium sulphate, $NiSO_4,(NH_4)_2SO_4,6H_2O$, saturated at 20–25°, a cast nickel block being used as anode and a thin polished sheet of pure nickel as cathode. The same process is used in **nickel-plating,** a thin layer of copper being first deposited on iron or steel goods. Nickel-plating is fairly easily dissolved by acids, *e.g.*, acetic acid.

Metallic nickel is a metal of a greyish-white colour, of sp. gr. 8·8, m.-pt. 1484°, very hard and malleable, and capable of taking a high polish. It is fairly resistant to air but gradually becomes dull; it is rendered passive by nitric acid. Nickel is magnetic below 360°. Finely-divided nickel absorbs 17 times its volume of hydrogen. It decomposes steam at a red heat: $H_2O + Ni \rightleftharpoons NiO + H_2$. At 2100°, nickel dissolves carbon, forming a **carbide,** Ni_3C, which decomposes on cooling.

Nickel salts.—Nickel dissolves slowly in dilute hydrochloric or sulphuric acid, evolving hydrogen, but dissolves readily in dilute nitric acid, a green solution of **nickel nitrate** being obtained. The green colour is that of the **nickel ion,** $Ni^{\cdot\cdot}$, and is shown by all the simple salts of nickel. On evaporation, green monoclinic crystals of $Ni(NO_3)_2,6H_2O$ are deposited. By heating these with concentrated sulphuric acid, dissolving the residue in water, and crystallising, green rhombic prisms of **nickel sulphate,** $NiSO_4,7H_2O$, separate, isomorphous with Epsom salts. If heated with the saturated solution at 54° these are converted into monoclinic crystals of $NiSO_4,6H_2O$. **Nickel chloride,** $NiCl_2,6H_2O$, is produced by dissolving the metal in *aqua regia,* and evaporating. On heating, the green crystals form the yellow anhydrous salt, $NiCl_2$.

Caustic soda throws down from solutions of nickel salts an apple-green precipitate of **nickel hydroxide,** $Ni(OH)_2$, insoluble in excess, but soluble in ammonia, forming a blue solution, containing two complex cations, $Ni(NH_3)_4^{\cdot\cdot}$ and $Ni(NH_3)_6^{\cdot\cdot}$, which are derived from bivalent nickel, and readily lose ammonia on heating (*cf.* cobalt). The **ammine** salts, *e.g.*, $Ni(NH_3)_6Cl_2$, $Ni(NH_3)_4SO_4,2H_2O$, may be obtained in blue crystals. On heating the hydroxide, **nickel monoxide,** NiO, is obtained as a grey mass, which is also formed on igniting the nitrate. By gentle ignition of the nitrate a black **sesquioxide,** Ni_2O_3, is formed, which liberates chlorine when dissolved in hydrochloric acid. A **superoxide,** NiO_4, is said to be formed by electrolysis, and a black hydrated **dioxide** is formed on passing chlorine through nickel hydroxide suspended in water. A green hydrated **peroxide,** NiO_2,xH_2O, or NiO,H_2O_2, is precipitated by adding cooled alcoholic potash to a mixture of nickel chloride and H_2O_2 cooled to − 50°. It readily liberates H_2O_2 by the action of acids. The black oxide may be O=Ni=O, the green oxide  $\mathrm{Ni}\Big<\begin{matrix}\mathrm{O}\\ | \\ \mathrm{O}\end{matrix}$.

Nickel carbonate, $NiCO_3,6H_2O$, is obtained in green crystals by adding nickel sulphate to a solution of sodium bicarbonate saturated with carbon dioxide. A green basic salt is precipitated from nickel salts by sodium carbonate.

Nickel sulphide, NiS, is thrown down as a black precipitate when ammonium sulphide is added to a nickel salt. It dissolves slightly in excess of the sulphide, forming a dark brown solution, from which it is precipitated by boiling, exposure to air, or addition of acids. Precipitated nickel sulphide readily oxidises in the moist condition on exposure to air, unless it has been precipitated by boiling a nickel salt with sodium thiosulphate (*cf.* p. 828), when it is much denser. It is insoluble in dilute acids, but dissolves in warm *aqua regia*. Other sulphides (Ni_2S, Ni_3S_2, Ni_3S_4) have been described.

Nickel carbonyl, $Ni(CO)_4$, is a colourless, strongly refracting liquid, prepared by passing carbon monoxide over reduced nickel at 30°. It boils at 43·2°, freezes at − 25°, and gives the normal molecular weight either as vapour or in solution. In the pure state it explodes at 60°, carbon being deposited: $Ni(CO)_4 = Ni + 2CO_2 + 2C$. A mixture of the vapour and air is explosive. Nickel carbonyl is best prepared under pressure, say, 100 atm., which is favourable to the right-hand side of the equilibrium: $Ni + 4CO \rightleftharpoons Ni(CO)_4$. At this pressure, decomposition does not occur even at 250°.

Nickel alloys.—Nickel is used in the manufacture of *nickel steel*, of crucibles and tubes, and alloyed with 25 per cent. of copper, for coinage (U.S.A., Germany, etc.) An alloy of four parts of copper to one part of nickel is used for coating rifle-bullets. *Nichrom*, an alloy of nickel and chromium, melts at a high temperature, and is used for electrical resistance heaters. *German silver* is the alloy 5 copper + 2 nickel + 2 zinc. Alloys used for resistance coils, etc., are:

platinoid: 60Cu + 24Zn + 14Ni + 1–2W.
constantan: 40Ni + 60Cu.
rheostan: 52Cu + 18Zn + 25Ni + 5Fe.

Separation of nickel and cobalt.—These two metals often occur together in analysis, and their separation may be effected by the formation of cobalticyanide (p. 1001), nickel forming only the bright red double salt, $Ni(CN)_2,2KCN$, or $K_2Ni(CN)_4,H_2O$, easily decomposed by acids. This is reduced by sodium amalgam to a lower cyanide, possibly NiCN. Nitrites form a double salt, $Ni(NO_2)_2,4KNO_2$, soluble in water, but if calcium salts are present a sparingly soluble yellow salt, $2KNO_2,Ca(NO_2)_2,Ni(NO_2)_2$, similar in appearance to a cobaltinitrite, may be formed. A solution of nitroso-β-naphthol in glacial acetic acid gives a brown precipitate with cobalt salts, but not with nickel. Characteristic reactions for nickel are the formation of a scarlet precipitate on addition of α-dimethylglyoxime to a solution containing nickel and ammonia or sodium acetate, and a yellow precipitate on addition of dicyanodiamide and then caustic potash to an acidified solution of a nickel salt.

Catalytic action of nickel.—Finely-divided nickel, obtained by reduction of the oxide in hydrogen, acts catalytically in many reactions involving the absorption of hydrogen. Thus, liquid fats containing glycerol esters of unsaturated fatty acids such as oleic (p. 206), if treated with pure hydrogen at 300–400° under pressure in presence of a little suspended nickel carbonate or borate, absorb hydrogen and form solid fats, *e.g.*, glyceryl palmitate. This process is used in the manufacture of *margarine.*

Estimation of nickel.—Nickel is precipitated from dilute solutions by adding a slight excess of dimethylglyoxime, and then ammonia drop by drop until the liquid smells slightly of ammonia. A bright red, crystalline precipitate of **nickel dimethylglyoxime,** $Ni(C_4H_7N_2O_2)_2$, is formed. This is filtered off, washed, dried, and weighed. The compound is stable, and sublimes at 120°. The reagent gives a colour with 0·01 mgm. of nickel.

EXERCISES ON CHAPTER XLIX

1. What are the minerals from which cobalt and nickel are obtained? Describe the production of nickel by the Mond process.

2. Describe briefly the properties of the oxides of cobalt and nickel.

3. How are cobalt and nickel separated in analysis?

4. How is nickel estimated? In what important respects do cobalt and nickel differ chemically?

5. Describe the properties of cobalt and nickel chlorides. What reactions occur when (*a*) ammonia is added to a solution of cobalt chloride, and the liquid is exposed to air, (*b*) excess of potassium cyanide is added to a cobalt salt and the liquid is boiled with acetic acid?

CHAPTER L

THE PLATINUM METALS

Platinum, Pt = 193·6.—The hieroglyphs on an Egyptian box, discovered at Thebes and dating from 7 B.C., were found by Berthelot to be composed of an alloy of platinum, iridium, and gold. Specimens of platinum seem first to have been brought to Europe by Charles Wood, and it was examined by Bishop Watson in 1750, further by Margraaf in 1757, and by Bergman in 1777. Platinum foil and wire were first made in 1772, and in 1806 they were sold in London, for chemical purposes, at 16*s*. an ounce. The metal now costs more than £20 per ounce. The normal production of the metal is about 9 tons per annum. The important Russian deposits in the Urals were discovered in 1823, and normally supply about 95 per cent. of the output, the remainder coming from California, Brazil, Borneo, and Australia, especially New South Wales. It is found in alluvial sands and gravels, and is separated by washing. The platinum concentrates consist of metallic grains which, in a specimen of Russian platinum, had the following composition:

Platinum	Iridium	Rhodium	Palladium	Gold	Copper	Iron	Osmiridium	Sand
76·4	4·3	0·3	1·4	0·4	4·1	11·7	0·5	1·4

Osmiridium is an alloy of osmium and iridium, with small amounts of other metals:

Osmium	Iridium	Platinum	Rhodium	Ruthenium
27·2	52·5	10·1	1·5	5·9

The gold is extracted by amalgamation, and the platinum metals are digested with *aqua regia*. Osmiridium remains undissolved. The solution is evaporated to dryness, and the residue heated to 125°. Palladium and rhodium form insoluble lower chlorides, PdCl and RhCl. On treating with water, **platinic chloride,** $PtCl_4$, and a little iridium chloride, $IrCl_4$, dissolve. The solution is acidified with hydrochloric acid and the **chloroplatinic acid,** H_2PtCl_6, precipitated with ammonium chloride as the sparingly ammonium salt, $(HN_4)_2PtCl_6$. The iridium remains in solution. On heating ammonium chloroplatinate it decomposes, leaving spongy platinum. If this is heated to redness and hammered, the sponge welds into a coherent mass of metal. The metal may also be fused in the oxy-hydrogen flame.

Properties of platinum.—Platinum is a greyish-white metal of high density, 21·4, and high melting point, 1753°. It can be welded at a bright red heat, and may be rolled or drawn into wire. Very fine wires (Wollaston wires), down to 0·001 mm., are drawn inside a silver sheath, which can be dissolved off in nitric acid, or by making the wire the anode in a solution of potassium argentocyanide. The metal is very resistant, but is attacked by carbon and phosphorus at a red heat, becoming brittle.

A smoky flame should not be used with platinum crucibles, nor magnesium pyrophosphate ignited along with the filter-paper, since in this case phosphorus is set free. Pure platinum is not attacked on heating in air, but the modern product loses weight appreciably and becomes grey and rough after heating. Easily reducible metals such as tin and lead readily alloy with platinum, causing it to fuse, and compounds of these metals must not be heated in platinum crucibles with filter-paper. Caustic alkalies also attack the metal in a fused state, but it is not attacked by the fused carbonates, nor by hydrofluoric acid. Fused lithium and magnesium chlorides. and potassium cyanide, attack platinum.

Pure platinum is not attacked by hot concentrated sulphuric acid, although the commercial metal dissolves slightly. It is dissolved by *aqua regia* on heating, especially if a large excess of concentrated hydrochloric acid is added. An alloy of platinum and lead dissolves in nitric acid, **platinum nitrate** being formed. On evaporating the solution in *aqua regia*, moistening the residue with concentrated hydrochloric acid, and re-evaporating, **chloroplatinic acid,** $H_2PtCl_6,6H_2O$, is obtained in reddish-brown, deliquescent crystals, commonly known as "platinic chloride."

Platinum has nearly the same coefficient of expansion as glass and may be sealed into the latter without causing cracking on cooling. The wires sealed into electric lamp bulbs were formerly of platinum, but have been replaced by manganin or Eldred's wire, which has a core of nickel steel, a jacket of copper, and an outer sheath of platinum. The metal is used in dentistry and in making jewelry, especially as a setting for diamonds.

It is used for contacts in electrical apparatus, and in large quantities as a catalyst in the manufacture of sulphur trioxide and the oxidation of ammonia. Tantalum has been proposed as a substitute for platinum in electrical contacts.

Platinum sponge is a grey, porous form obtained by heating ammonium chloroplatinate. **Platinum black** is a finely-divided powder obtained by reducing a solution of chloroplatinic acid by zinc, or with sodium formate solution. These forms are very active catalytically. Alcohol is oxidised by platinum black, on account of its occluded oxygen, to aldehyde, and a mixture of oxygen and hydrogen is exploded.

Platinised asbestos is made by soaking asbestos fibres, previously boiled with concentrated hydrochloric acid, in platinic chloride solution, drying, and heating in a crucible with a little ammonium chloride, or reducing with sodium formate solution. **Colloidal platinum** is formed as a brown solution by causing small electric arcs to pass repeatedly between platinum wires under water, or by reducing a solution of platinic chloride with hydrazine in presence of sodium lysalbate, a protective colloid. The colloidal solution is a catalyst (see H_2O_2).

EXPT. 341.—Heat a spiral of platinum wire in a Bunsen flame. Turn off the gas until the wire ceases to glow. Turn on the gas again. The wire becomes red hot and ignites the gas (see p. 198).

EXPT. 342.—Heat a spiral of platinum wire to redness and suspend it in a flask containing a little alcohol. The wire continues to glow, and pungent vapours of aldehyde, C_2H_4O, are formed.

Compounds of platinum.—Platinum forms **two series of compounds:** the **platinous compounds,** PtX_2, and the more important **platinic compounds,** PtX_4.

Chloroplatinic acid, $H_2PtCl_6,6H_2O$, the preparation of which has been described, is a strong dibasic acid; it gives with silver nitrate a yellow precipitate of silver chloroplatinate, Ag_2PtCl_6; the chloroplatinates of the alkali-metals have been described (p. 797). The acid therefore gives the ion $PtCl_6''$; on electrolysis this migrates to the anode, although metallic platinum is deposited on the cathode as a result of the reducing action of the hydrogen liberated.

On heating potassium chloroplatinate, a residue of platinum and potassium chloride is left: $K_2PtCl_6 = 2KCl + Pt + 2Cl_2$. Ammonium chloroplatinate, $(NH_4)_2PtCl_6$, leaves a residue of pure platinum.

Platinic chloride, $PtCl_4$, is obtained as a reddish-brown, crystalline mass when chloroplatinic acid is heated at 369° in chlorine, or 165° in hydrochloric acid. At 435°, in chlorine, the greenish-black **trichloride,** $PtCl_3$, is obtained, and at 580°, brownish-green **platinum dichloride,** $PtCl_2$. The dichloride is also obtained by heating the tetrachloride at 250–300°. Platinum tetrachloride dissolves in water to form a yellowish-red solution, which appears to contain a complex acid, $[PtCl_4(OH)_2]H_2$, since it forms a silver salt, $[PtCl_4(OH_2)]Ag_2$. Crystals of $PtCl_4,5H_2O$ may be obtained. Platinum dichloride is insoluble in water, but dissolves in hydrochloric acid to form a dark-brown **chloroplatinous acid,** H_2PtCl_4, which is also obtained by the action of stannous chloride on chloroplatinic acid.

When sodium carbonate is added to chloroplatinic acid solution, and the residue after evaporation extracted with acetic acid, reddish-brown **platinic hydroxide,** a complex compound, $H_2[Pt(OH)_6]$, remains. This dissolves in hydrochloric acid to form $H_2[Pt(OH)_2Cl_4]$; silver nitrate gives with the solution $Ag_2[Pt(OH)_6]$. On gentle heating, $H_2[Pt(OH)_6]$ leaves black **platinum dioxide,** PtO_2. **Platinum trioxide** is formed when a solution of potassium platinate, $K_2[Pt(OH)_6]$, in caustic potash is electrolysed and the deposit on the anode, $K_2O,3PtO_3$, treated with cold acetic acid; it is a brown powder which does not decompose H_2O_2.

Alkalies precipitate from solutions of platinochlorides black **platinous hydroxide,** $Pt(OH)_2$, probably complex, $H_2[Pt(OH)_4]$, soluble in hydrochloric acid. This has no acidic properties; on gentle heating it forms black **platinous oxide,** PtO. **Potassium platinochloride,** K_2PtCl_4, is obtained by warming a paste of potassium chloroplatinate, K_2PtCl_6, with cuprous chloride. It forms dark red crystals, used in photography.

Paper is impregnated with a mixture of K_2PtCl_4 and ferric oxalate. On exposure to light, the ferric oxalate is reduced to ferrous oxalate, and if the paper is developed in a solution of potassium oxalate a grey deposit of platinum is formed on the reduced parts ("platinotype.")

Sulphuretted hydrogen throws down from H_2PtCl_6 a black precipitate of **platinic sulphide,** PtS_2, soluble in yellow ammonium sulphide to a dark-brown solution of a **thioplatinate,** $(NH_4)_4Pt_3S_6$. Platinous salts give **platinous sulphide,** PtS.

Potassium iodide does not give with chloroplatinic acid a precipitate of potassium iodoplatinate, but a dark red clear solution. On heating, this deposits black **platinic iodide,** PtI_4, soluble in alcohol. When digested with hydriodic acid this forms **iodoplatinic acid,** H_2PtI_6, crystallising in black needles. Platinic iodide decomposes into iodine and platinum at 130°. **Platinous iodide,** PtI_2, is obtained as a black powder by heating platinous chloride with potassium iodide solution.

Complex platinum compounds.—Numerous complex compounds of platinum are known. The **platinammines** contain molecules of ammonia co-ordinated with the metal atom as in the cobaltammines (p. 1001); two series exist, corresponding with bivalent and quadrivalent platinum. **Barium platinocyanide,** $BaPt(CN)_4,4H_2O$, is a lemon-yellow powder used for fluorescent screens in *X*-ray work. Baryta-water and hydrocyanic acid are added to chloroplatinic acid, the solution warmed, and treated with sulphur dioxide till colourless. $BaSO_4$ is filtered off and the filtrate crystallised.

Palladium, Pd = 105·9.—When potassium cyanide is added to the solution of native platinum in *aqua regia* a pale yellow precipitate of **palladious cyanide,** $Pd(CN)_2$, is obtained, which on ignition leaves metallic **palladium** (Wollaston, 1803). The metal oxidises superficially when heated in air, becoming covered with a blue film of **monoxide,**

PdO. Palladium dissolves in dilute nitric acid, forming **palladious nitrate,** $Pd(NO_3)_2$, and in *aqua regia,* forming **chloropalladic acid,** H_2PdCl_6. Potassium iodide throws down from this a black precipitate of **palladious iodide,** PdI_2, soluble in excess to a brown solution. The tendency to formation of palladious compounds is noteworthy. The absorption of hydrogen by palladium has been considered (p. 194).

Osmium, Os = 189·4, **and Iridium, Ir** = 191·6.—These two metals are contained in *osmiridium* (p. 1006). If this is fused with sodium chloride in chlorine, **osmic chloride,** $OsCl_4$, volatilises. The solution of the residue in hydrochloric acid is treated with hydrogen; platinum and **ruthenium** are deposited. When more hydrogen is passed through the decanted green liquid, **iridium** is thrown down (Tennant, 1804).

Iridium is very hard, and is used for the tips of gold pens. Iridium crucibles resist the action of carbon, phosphorus, and *aqua regia.* The standard metre of Paris was constructed by Johnson and Matthey, in London, from an alloy of 90 parts of platinum and 10 parts of iridium. The same alloy is used, together with pure platinum, in constructing thermocouples for the measurement of high temperatures. Since iridium volatilises above 1000°, an alloy of platinum and rhodium is used at higher temperatures.

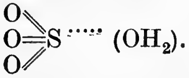
When osmium tetrachloride is precipitated with ammonium chloride, and the **ammonium osmichloride,** $(NH_4)_2OsCl_6$, heated in absence of air, metallic **osmium** is left. The metal burns when heated in air or oxygen, forming the volatile **osmium tetroxide,** OsO_4, commonly called "osmic acid." This substance has a very irritating odour resembling bromine, and attacks the eyes. It is easily reduced by organic matter to a black powder of hydrated dioxide, OsO_2: solutions of osmic acid are used in microscopy for staining fat globules. The fluoride OsF_8 is known.

Ruthenium, Ru=100·9, **and Rhodium, Rh**=102·1.—When the precipitate of platinum and ruthenium obtained as described in the preceding section is fused with potassium nitrate and caustic potash, **potassium ruthenate,** K_2RuO_4, is formed. The orange-yellow solution of this, when distilled in a current of chlorine, gives volatile **ruthenium tetroxide,** RuO_4, similar to OsO_4.

Rhodium is contained in the *aqua regia* solution of the crude platinum after precipitation with ammonium chloride. If ammonia is added and the solution evaporated and ignited, metallic rhodium is left (Wollaston, 1804).

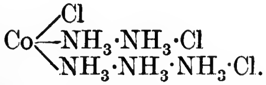
WERNER'S THEORY OF VALENCY.

Werner's theory of complex compounds.—The formation of so-called **molecular compounds** is explained on Werner's theory by an extension of the hypothesis of residual affinity described on p. 252. In compounds such as H_2O and SO_3 the **principal valencies** of the atoms are saturated, and the molecules are incapable of uniting with another univalent atom. By reason of the **residual valencies,** however, the two molecules may enter into combination, forming probably first an association held together by residual valencies :



When association has occurred, the affinities may re-distribute themselves uniformly, with the formation of radicals, such as SO_4, having affinities capable of binding univalent atoms, such as 2H to form H_2SO_4. According to Werner, these hydrogen atoms, for instance, exist outside the sphere of the complex radical SO_4, and are therefore easily split off in solution as ions. In this way the curious behaviour of the chlorine atoms in chloroplatinic acid, H_2PtCl_6, is explained. This compound does not give Cl' ions, but $H^{\cdot}$ and the complex anion $PtCl_6''$. In this case, the six chlorine atoms are considered to be directly combined with the metal atom in the central complex, whilst the two hydrogen atoms outside the nucleus are readily ionisable. In the same way, the ionisable hydrogen of HCl, when this combines with ammonia, is associated with the nitrogen atom in the nuclear group NH_4; the Cl atom, existing outside the nucleus, is ionisable. The constitution of such complex compounds as the cobaltammines was formerly explained (Blomstrand, 1869) by the attachment of ammonia molecules in open chains to the metal atom, in virtue of the quinquevalent character of nitrogen :—

e.g.,



The existence of isomers may be expressed by varying the positions of the different groups. This theory is no longer accepted, as it fails to account for many known cases of isomerism.

Alphonse Werner (1893) supposed, on the contrary, that in these compounds the metal atom is directly united with the non-ionisable groups such as NH_3, NO_2 (in cobaltinitrites), etc., which form part of the complex radical, and are not ionised in solution, by what he calls the **supplementary valencies** of the metal atom. (These correspond with the "residual valencies" of p. 253.) The **principal valencies** of the central atom, which are active in the ordinary ionisable compounds, *e.g.*, $CoCl_3$, are then free to attach other ionisable radicals. The complex formed by the supplementary valencies may be regarded as forming a **nucleus** outside which the ionisable radicals are attached. The mode of attachment of the radicals outside the nucleus is left indefinite by Werner, who places their symbols outside square brackets enclosing the complex nucleus, *e.g.*,

$$\overset{\text{III}}{[\text{Co}}(\text{NH}_3)_6]\text{Cl}_3 \rightleftharpoons \overset{\text{III}}{[\text{Co}}(\text{NH}_3)_6]^{\cdots} + 3\text{Cl}'.$$

The atoms or radicals in the complex nucleus are said to be **co-ordinated** with the metal atom; the number of such groups is, in the majority of cases, six, but may be four, as in the complex platinous compounds, $[\overset{\mathrm{II}}{\mathrm{Pt}}(\mathrm{NH_3})_4]\mathrm{Cl_2}$. This number, *e.g.*, 4 or 6, is called the **co-ordination number** for the series of compounds.

The valency of the nucleus is equal to the principal positive valency of the metal atom when the latter is co-ordinated only with groups, such as NH_3 or H_2O, which are usually regarded as saturated; but if negative radicals such as Cl, which may be considered as ions, are in the complex nucleus, the positive valency of the metal atom is reduced by one unit for each such radical present in the nucleus, and if the number of these radicals exceeds the principal valency of the metal atom, the complex becomes as a whole negative, and unites with a corresponding number of positive atoms or radicals.

E.g., in the compounds of quadrivalent platinum, the complex $[\overset{\mathrm{IV}}{\mathrm{Pt}}(\mathrm{NH_3})_5\mathrm{Cl}]$ will have a positive valency of $4-1=3$, and will therefore form $[\overset{\mathrm{IV}}{\mathrm{Pt}}(\mathrm{NH_3})_5\mathrm{Cl}]\mathrm{Cl_3}$, whilst the complex $[\overset{\mathrm{IV}}{\mathrm{Pt}}(\mathrm{NH_3})\mathrm{Cl_5}]$ will have a valency of $4-5=-1$, and will therefore form $[\overset{\mathrm{IV}}{\mathrm{Pt}}(\mathrm{NH_3})\mathrm{Cl_5}]\mathrm{K}$. In the former compound three-quarters of the chlorine, being outside the nucleus, will be ionisable, and may be precipitated as silver chloride; in the latter compound all the chlorine is in the nucleus, is non-ionisable, and cannot be precipitated as silver chloride:

$$[\mathrm{Pt(NH_3)_5Cl}]\mathrm{Cl_3} \rightleftharpoons [\mathrm{Pt(NH_3)_5Cl}]^{\cdot\cdot\cdot} + 3\mathrm{Cl}'$$
$$[\mathrm{Pt(NH_3)Cl_5}]\mathrm{K} \rightleftharpoons [\mathrm{Pt(NH_3)Cl_5}]' + \mathrm{K}^{\cdot}.$$

Isomerism of complex compounds.—Werner's theory predicts the existence of several kinds of **isomers** of complex compounds, and in a great many cases these isomers have been prepared. At first the theory was in many directions speculative, and encountered opposition, but with the actual isolation of many of the formerly hypothetical compounds, the existence of which could not have been foreseen except by the theory, the value of the latter has become recognised. At the same time, it must be admitted that the conceptions used in Werner's theory, *e.g.*, those of "supplementary valencies," and of the "positions inside and outside the nucleus," are vague, but in this respect are at no disadvantage in comparison with the modern theory of the structure of organic compounds. In both cases, the **cause of valency** is unknown.

If the cause of valency is identified with electrical forces, the effect of substitution of electrically neutral molecules, such as NH_3, by ions, such as Cl, is explained; the latter exert electrical forces outside the complex, and the repeated addition of negative atoms to the complex changes the electrochemical character of the latter in the manner described.

Seven types of isomerism are possible on Werner's theory :—

(1) *Structural isomerism in the nucleus* : *e.g.* :

$$\left[\begin{matrix}\mathrm{NO} - \mathrm{O} \\ \mathrm{NO} - \mathrm{O}\end{matrix}\ \mathrm{Co\ en_2}\right] \text{ and } \left[\begin{matrix}\mathrm{O_2N} \\ \mathrm{O_2N}\end{matrix}\ \mathrm{Co\ en_2}\right]$$

where *en* represents ethylenediamine, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, with two supplementary valencies.

(2) *Ionisation isomerism,* in which the positions inside and outside the nucleus are interchanged, *e.g.*,

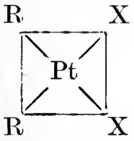
$$[Co(SO_4)(NH_3)_5]Br \text{ and } [CoBr(NH_3)_5]SO_4.$$

The first splits off a Br′ ion ; the second the ion SO_4''.

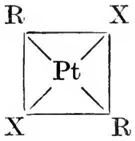
The valencies of the two complex radicals are in accordance with the theory.

(3) *Geometrical isomerism*, due to the different arrangement of the atoms and groups in space about the central metal atom :—

(*a*) In one plane :—



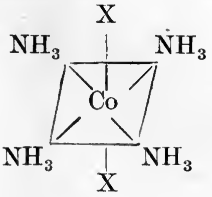
cis-isomer



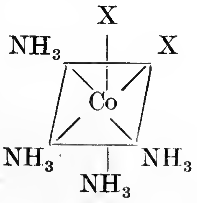
trans-isomer

A *cis*-form contains adjacent atoms of the same element ; in a *trans*-isomer these are arranged in opposite positions.

(*b*) Compounds of the type $[MeR_4X_2]$ can exist in *two* forms, which are represented by placing the metal atom (Me) at the centre of a regular octahedron, with its six supplementary valencies directed to the six corners. (The possibility that the atoms are arranged in a plane hexagon is excluded because this would lead to *three* possible isomers, whereas only two are known.) The two (univalent) nuclei of the compounds $[Co(NH_3)_4X_2]X$ are of this type : —



trans



cis

X = Cl, etc.
(negative)

The *cis*-modifications are distinguished from the *trans*-modifications by their capacity for ring-formation.

(4) *Co-ordination isomerism,* depending on the different arrangements of groups in two nuclei in combination :

$$[Cr(NH_3)_6]\cdot[Cr(SCN)_6] \text{ and } [Cr(NH_3)_4(SCN)_2]\cdot[Cr(NH_3)_2(SCN)_4].$$

(5) *Co-ordination polymerism* :

$$[Cr(NH_3)_3(SCN)_3] \text{ and } [Cr(NH_3)_5(SCN)]_3\cdot[Cr(SCN)_6]_2.$$

(6) *Hydration isomerism* : the groups NH_3, Cl, etc., in the nucleus, may be replaced by water, H_2O, forming *aquo-compounds* :

$$\underset{\textit{ammine compound.}}{[Cr(NH_3)_6]Cl_3} \rightarrow [Cr(H_2O)(NH_3)_5]Cl_3 \rightarrow \dashrightarrow \underset{\textit{aquo-compound.}}{[Cr(H_2O)_6]Cl_3}$$

In such compounds, the ionisable Cl may pass into the nucleus :

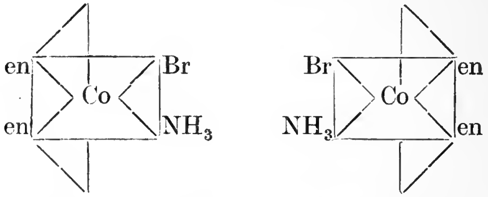
$$[Cr(H_2O)(NH_3)_5]Cl_3 = [CrCl(NH_3)_5]Cl_2 + H_2O$$

It then ceases to be ionisable. The two green chromic chlorides (p. 951) are compounds of this type :

$$[CrCl(OH_2)_5]Cl_2 + H_2O \text{ and } [CrCl_2(OH_2)_4]Cl + 2H_2O.$$

The blue modification is $[Cr(OH_2)_6]Cl_3$.

(7) *Optical isomerism* : the most convincing argument in favour of Werner's theory is the existence of **optical isomers.** These arise when two compounds have such arrangements of the atoms or groups in space about the central atom that one structure is the mirror-image of the other :



(The bivalent group *en* engages *two* valencies of the metal atom, one axial and one in the plane.)

The existence of optical isomers cannot be detected by the chemical properties of the compounds : these are identical in both cases. All the physical properties, such as solubility, density, etc., with one exception, are also identical. The exception is the behaviour of the compounds to **polarised light.** A ray of light is separated by a Nicol's prism, or other arrangement, into two rays which are complementary in the sense that the vibrations constituting the light occur in directions at right-angles in the two cases. Each of these rays, exhibiting a unilateral vibration, is called **polarised.** When a polarised ray passes through a solution of an optical isomer, the plane in which the vibrations occur is rotated, so that if the entering ray is extinguished by a

Nicol prism with its axis at right angles to the plane of polarisation, the ray after passing through the solution is not totally extinguished, showing that the plane of polarisation is no longer at right angles to the axis of the prism. It is found that one isomer rotates the plane of polarisation to the right, or is **dextrogyrous**, whilst the other isomer rotates the plane of polarisation to an equal extent to the left, or is **lævogyrous.** Optical activity is always associated with **asymmetric structure** of the molecules of the two compounds, *i.e.*, the spacial configurations of the two molecules are not superposable, but are related one to the other as an object and its image in a mirror, or as the right and left hand.

EXERCISES ON CHAPTER L

1. Which elements are included in the group of " Platinum Metals " ? What are their general chemical properties, and to what uses are they applied ?

2. Starting with platinum foil how would you prepare : (*a*) platinum sponge, (*b*) colloidal platinum, (*c*) platinous chloride, (*d*) chloroplatinic acid, (*e*) potassium platinate ? Describe briefly the properties of these substances.

3. Describe briefly how the metals found in native platinum may be separated. How would you purify platinum from (*a*) palladium, (*b*) iridium ?

4. What is osmic acid ? How is it prepared from osmiridium, and for what purpose is it used ? How has the maximum valency of osmium been established ?

5. Chloroplatinic acid was added to a solution of ammonium chloride ; the precipitate after ignition left a residue of 0·4752 gm. of platinum. What weight of ammonium chloride was contained in the solution ?

6. What is Werner's theory of complex compounds ? Explain the meaning of : principal valency, supplementary valency, central sphere, co-ordination number, *cis-trans*-isomerism, optical isomers, co-ordination isomerism.

CHAPTER LI

THE RADIO-ELEMENTS AND THE STRUCTURE OF THE ATOM

Cathode rays.—The phenomena of the **electric discharge in gases** are described in text-books of physics (*e.g.*, Hadley: "Magnetism and Electricity for Students." Macmillan). At very low pressure (0·01 mm.) an electrical discharge proceeds as a blue glow from the cathode in the exhausted tube, in a course normal to the cathode, and independent of the position of the anode, producing a green fluorescence where it strikes the glass. These **cathode rays,** proceeding from the cathode, were discovered by Crookes in 1870; they are deflected by a magnet, showing that they are electrically charged. Perrin was able to demonstrate directly that they were negatively electrified, and by measuring the deflection produced by magnetic and by electric fields, Sir J. J. Thomson (1897) found the ratio of the charge to the mass of the particles, e/m, to be $1{\cdot}2 \times 10^8$ cmb. per gm.; recent determinations give $1{\cdot}772 \times 10^8$ cmb. per gm. The corresponding ratio for the hydrogen ion in electrolysis (p. 282) is $\mathbf{F} = 9{\cdot}58 \times 10^4$; the value for cathode rays is 1850 times this. Of the two possibilities: (i) the charges are the same, but the mass of the cathode particle is 1/1850 that of the hydrogen atom; (ii) the masses are the same, but the charge on the cathode particle is 1850 that on the hydrogen ion, experiment has decided in favour of the first. The cathode rays are free **negative electrons** (p. 281). The cathode rays have the same value of e/m, no matter what is the material of the electrodes or the gas in the bulb; they are also emitted by the action of ultra-violet light on metals, and in many chemical reactions. This evidence points to electrons being *a common constituent of all atoms.*

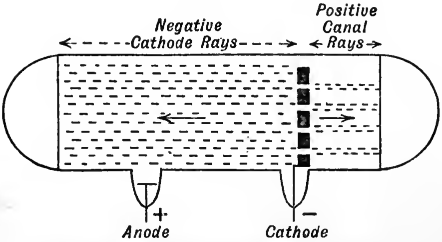


FIG. 424.—Cathode and Positive Rays.

Positive rays.—If the cathode in the tube is perforated, luminous rays pass backwards through it (Goldstein, 1886); by their deflections in magnetic and electric fields these are found to consist of positive particles of atomic size (Fig. 424). The **positive rays** have been investigated by Sir J. J. Thomson, using the apparatus shown in Fig. 425. Some of the particles were found to be uncharged.

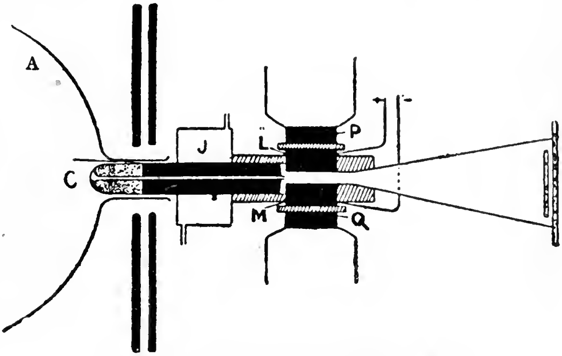


Fig. 425.—Thomson's Positive Ray Apparatus.

An electric discharge is passed through the rarefied gas in a bulb, *A*, about 20 cm. diameter. The cathode, *C*, is an aluminium rod with a rounded end, pierced by a very fine copper tube, through which a fine pencil of rays passed between the plates, *L* and *M*, which are connected with the positive and negative poles of a battery, and the pole pieces, *P* and *Q*, of an electromagnet. The cathode is cooled by a water-jacket, *J*. The rays are deflected by the combined electric and magnetic fields, in two directions at right angles to each other, and the separated pencils of rays then strike a photographic plate. The rays characterised by definite values of e/m are sorted out into a series of parabolas on the plate, which are seen in Fig. 426. By measuring these, the values of m/e and thence, if the charges e are assumed, the masses, m, of the particles can be calculated. In atmospheric nitrogen the following results were obtained.

m/e.		**Nature of Particle**
200	Hg^{+}	Mercury atom with single charge.
100	Hg^{++}	Mercury atom with two charges.
67	Hg^{+++}	Mercury atom with three charges.
44	CO_2^{+}	Molecule of carbon dioxide with single charge.
39	A^{+}	Argon atom with single charge.
28	N_2^{+}	Nitrogen molecule with single charge.
20	Ne^{+}	Neon atom with single charge.
15·9	O^{+}	Oxygen atom with single charge.
14	N^{+}	Nitrogen atom with single charge.
12	C^{+}	Carbon atom with single charge.
7	N^{++}	Nitrogen atom with two charges.

X-rays.—When the cathode rays strike the positive electrode, or anti-cathode, in the bulb, they give rise to a penetrating radiation which passes outside the tube. This is capable of penetrating freely through paper, wood, aluminium, and flesh, but is largely absorbed by lead, platinum, glass, or bone. These so-called **X-rays** (Röntgen, 1895) have now been produced sufficiently penetrating to pass through two inches of steel. They affect a photographic plate, cause fluorescence when they fall on substances such as barium platinocyanide, and render a gas conducting or produce **ionisation** in the latter, free electrons and positively charged atoms being formed. For this reason, a gold-leaf electroscope rapidly loses its charge when exposed to *X*-rays, since the surrounding air conducts away the charge. The *X*-rays have been shown to consist of **ether waves** similar to light, but of much smaller wave-length. The latter depends on the composition of the positive anti-cathode, or "target," bombarded by the cathode rays and from which the *X*-rays proceed.

FIG. 426.—Positive Ray Parabolas.

Bragg's researches on X-rays and crystals.—For a long time it was not possible to obtain diffraction of *X*-rays by matter, since the wave-lengths are very much smaller than those of light. Friedrich, Knipping, and Laue (1912) showed that *X*-rays suffer diffraction in passing through **crystals,** and the further work of Sir W. H. Bragg indicated that they suffered reflexion from crystal surfaces at definite angles of incidence in the same way as light from a diffraction grating (Bragg: "X-rays and Crystal Structure," Bell, 1920).

If the primary *X*-rays are homogeneous, *i.e.*, all of the same wave-length, the series of directions along which reflexion will occur are obtained by giving the values 1, 2, 3, . . . to n in the general equation: $2d \sin \theta = n \lambda$, where λ is the wave-length. In the ordinary diffraction grating, d is the space between the rulings; in the case of *X*-ray reflexion from crystals, Bragg identifies d

with the distance between planes in the crystal corresponding with the densest arrangement of the atoms. These planes correspond with the symmetry of the crystal (p. 433). It is evident that an examination of X-ray spectra provides the means of exploring the atomic architecture of crystals, and in this direction the method has been applied with great skill and success by W. H. and W. L. Bragg.

The apparatus used is shown in Fig. 427. The rays from the anticathode of the X-ray bulb are constricted to a narrow pencil by the lead slits, A and B, and impinge on the crystal, C, mounted on a rotating arm, V, moving over a graduated circle. The reflected beams are received in an ionisation chamber, I, also pivoted at the centre of the X-ray spectrometer, and render the gas contained in the chamber, usually sulphur dioxide, a conductor of electricity. The intensity of the current passing through the gas, measured by an electroscope, indicates the positions of reflexion from the crystal. The ionisation occurs with homogeneous X-rays only at certain definite angles corresponding with the different order of spectra given by the equation: $2d \sin \theta = n\lambda$. In the graph of the current against the angle of incidence, peaks occur corresponding to definite wave-lengths in the X-rays, and these are repeated as the spectra of different orders are passed over. In the case of a platinum anti-cathode, for instance three peaks are found, showing that the X-radiation of platinum is a mixture of three characteristic wave-lengths. These reappear whatever the nature of the crystal used for reflexion.

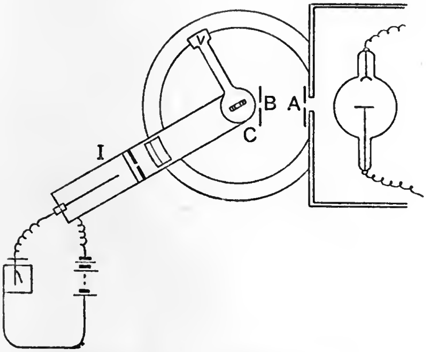


FIG. 427.—Bragg's X-ray Spectrometer.

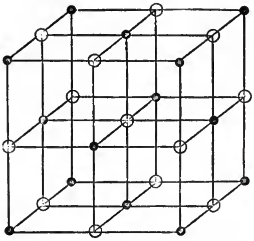


FIG. 428.—Arrangement of Atoms in Sodium Chloride Crystal.

By making use of the principle that the intensity of the radiation scattered from an atom is proportional to the number of electrons in the atom, and thus according to the modern theory of atomic structure (p. 1035) to the atomic weight of the atom, it was possible to show that the two strong reflexions from potassium chloride were due to the atoms K and Cl, of approximately equal weight, whilst the strong and weak reflexions from sodium chloride were due to the Cl and Na atoms, respectively. In this way the structure of such crystals was made out to be that shown in Fig. 428, the metal atoms being represented by dots and the chlorine atoms by circles. The constituent particles of crystals of salts are not, therefore, the chemical molecules, such as NaCl, but the atoms (or ions) Na and Cl, arranged in a definite manner.

MADAME CURIE

Radioactivity.—In 1896, Becquerel found that uranium salts were capable of affecting a photographic plate through a layer of black paper, and also of discharging an electroscope. Thorium compounds were found by Schmidt and by Mme. Curie in 1898 to possess similar properties. The substances were called

radioactive, from their property of emitting radiations of the kind described. In the study of radioactivity the following methods are available :

(1) The action on a **photographic plate.**

(2) The **phosphorescence** produced in platinocyanides, willemite (zinc silicate), kunzite, and Sidot's spar (zinc sulphide).

(3) The **ionisation of gases** produced by the rays.

The most convenient is the third method ; the ionisation, which renders the gas conducting, is detected and measured by the **gold-leaf electroscope** (Fig. 429). The strip of gold-leaf, *G*, is attached to the vertical rod, *R*, supported by a horizontal rod, *K*, insulated on blocks of sulphur, *S*, and terminating in a metal plate, *B*. Below this is a second metal plate, *A*, on which the material to be tested is placed. The motion of the gold-leaf is observed through a micrometer eyepiece, the leaf being given a charge through the wire, *M*, which is insulated in a sulphur stopper, *S*, and can be swung away from the rod, *R*, when the latter is charged. If the substance, *C*, is radioactive, the air between the plates *A* and *B* is rendered conducting, owing to the production of positive and negative **gaseous ions,** and the charge leaks away at a rate which may be observed by the fall of the gold-leaf. The electroscope, as applied to the detection of radioactive substances, is much the most sensitive instrument known, since 10^{-12} gm. of material can readily be recognised.

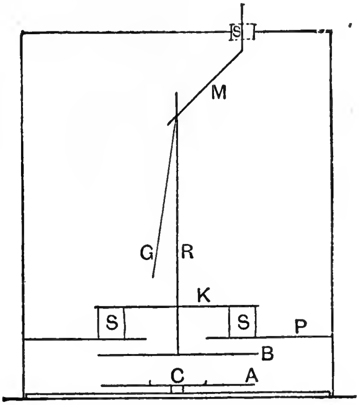


FIG. 429.—Gold-Leaf Electroscope.

Radium.—By means of an electroscope, Mme. Curie found that the native uranium ore, *pitchblende,* was more active, for the same weight of uranium, than a purified uranium salt, and she suspected that this was owing to the presence of a new element in the ore which was much more radioactive than uranium. She succeeded in isolating a trace of an intensely active substance from the pitchblende ; this was an impure salt of a new element, **radium.** It possessed an activity a million times that of uranium. In highly purified specimens this activity is found to be doubled.

The separation of the radium from pitchblende is a laborious process. Radium and barium chlorides are separated by a long series of fractional crystallisations (p. 908); with the bromides eight crystallisations suffice for the separation.

An important source of radium compounds is the *carnotite* of Colorado (p. 958). This contains 5–10 mgm. of Ra per ton. The material is boiled with 40 per cent. nitric acid, and the hot filtered solution deposits barium and radium sulphates on cooling. These are reduced to sulphides by heating with carbon, the sulphides are dissolved in hydrobromic acid, and the salts fractionally crystallised.

Radium compounds are isomorphous with those of barium; the ratio of chlorine to radium in the chloride is 35·2 : 112·15, so that on the assumption that the formula is $RaCl_2$, the atomic weight of radium is 224·3. It is an element of the group of alkaline-earth metals. The crystals of the pure salts are colourless; if they contain barium they are pink. The solution in water evolves oxygen and hydrogen continuously, and the solid salts ozonise air. In the dark they shine with a green phosphorescent glow. In accordance with the behaviour of the metals of its group, radium sulphate is even less soluble than barium sulphate, since the element has a higher atomic weight. In the Bunsen flame radium compounds give a fine carmine tint, and the spectrum is analogous to those of the other elements in the group.

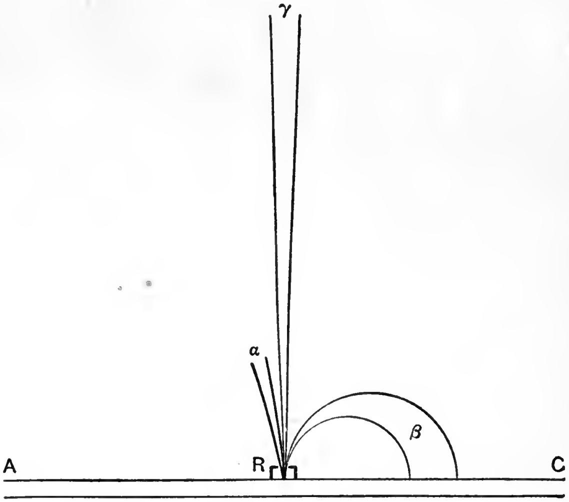


FIG. 430.—Magnetic Deflection of Rays from Radium.

Metallic radium was obtained by Mme. Curie in 1910 by electrolysing a solution of the chloride with a mercury cathode, and separating the mercury from the amalgam by distillation. It is a white metal, m.-pt. 700°, which rapidly tarnishes in the air, and decomposes water with evolution of hydrogen.

α-, β-, **and** γ-**Rays**.—By interposing sheets of metal foil and superposing powerful magnetic fields, in the electroscopic method (p. 1021), it was found that radium emits **three kinds of rays** (Fig. 430) :—

1. The α-**rays** : positively charged particles, easily absorbed by thin metal foil, and having a limited range in air (7·06 cm. when emitted from RaC).
2. The β-**rays** : negatively charged particles, identical with free negative electrons (p. 281), emitted with speeds approaching the velocity of light, and often capable of penetrating thin sheets of aluminium.
3. The γ-**rays** : are not deflected by magnetic fields, and consisting of ether waves identical with very short X-rays (wave-length, $1{\cdot}3 \times 10^{-7}$ to 7×10^{-10} mm.), are capable of penetrating several cm. of lead.

The deflections produced by a magnetic field are seen in Fig. 430 to be in opposite directions with the α- and β-rays: the γ-rays are undeflected. The α-rays have a shorter range than the β-rays.

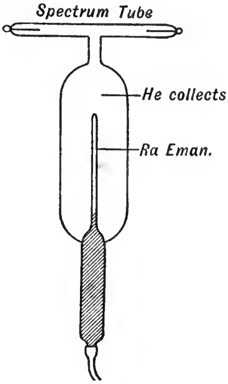


FIG. 431.—Production of Helium from Radium Emanation.

The α-rays.—The phosphorescent effects of radium are mainly due to the α-**rays**, which, on account of their relatively large mass, possess considerable kinetic energy. In the **spinthariscope** (p. 267) the impact of each α-particle on the screen produces a bright flash and in this way a direct counting of the particles is possible. The α-rays have been studied especially by Sir Ernest Rutherford, who found for them the value $e/m = 5{\cdot}07 \times 10^4$ cmb./gm., almost exactly half that for the hydrogen ion in electrolysis. They may, therefore, consist of atoms of weight 2 with one positive unit charge, or atoms of weight 4, *i.e.*, helium atoms, with two unit charges. By sealing radium emanation (p. 1025) in a thin glass tube, Rutherford and Royds (1909) found that the α-particles escaped into an outer vacuous tube fitted with electrodes, and on passing a discharge through the latter the helium spectrum was detected (Fig. 431). The α-particle was thus independently found to consist of an atom of weight 4, or a **helium atom**, with two unit positive charges, or as is now believed a helium atom which has lost two negative electrons. The speed with which α-particles are emitted by radium is about 2×10^9 cm. per sec., hence the kinetic energy of an α-particle is $1{\cdot}34 \times 10^{-5}$ erg, or $2{\cdot}2 \times 10^9$ times that of a gas molecule at 0° (p. 268). It is this large energy which accounts for the phosphorescent effects, and for the heat evolved by radium, which amounts to 118 gm. cal. per gm.

of radium per hour. The urgent question when the properties of radium were gradually unfolded was to account for this continuous production of energy without any appreciable diminution in the amount of radioactive substance, or of its activity.

The α-particles passing through air produce gaseous ions, which can act as nuclei for the deposition of moisture. If a particle of radium is contained in a vessel of air saturated with moisture and the air is suddenly cooled by expansion, the paths of the rays become visible in lines of droplets of water, which can be photographed. In this way C. T. R. Wilson obtained the photographs shown in Fig. 432. The paths of two single α-rays are shown in Fig. 433. It will be seen that they end abruptly. The rays must have passed through several atoms of the gas in their track, without suffering stoppage or appreciable deflection, but the vertical track shows a large deflection at its end, and a very small spur is seen going off in the other direction. The latter probably represents the track of the atom of gas which has stopped the α-particle ; this has

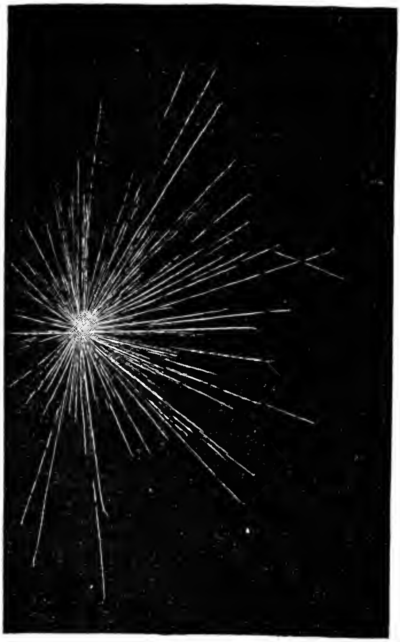


FIG. 432.—Tracks of α-rays.

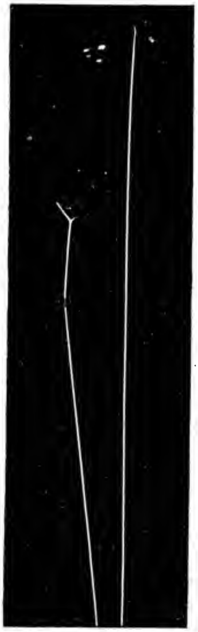


FIG. 433.—Tracks of two α-rays (enlarged).

imparted to it a recoil velocity, but on account of its larger mass it is quickly stopped by collision.

The tracks of β-rays, photographed in the same way, are shown in Fig. 434. These indicate deflections by collisions with relatively massive gas particles. The tracks produced by γ-rays are shown in Fig. 435. These are really produced by secondary β-rays, or electrons shaken out of the gas atoms by the γ-rays.

FIG. 434.—Tracks of β-rays.

Radium emanation.—It was soon noticed that some kind of gas is continually evolved from radium, which may be swept away by a current of air and is condensed in a tube cooled in liquid air. By measuring the rate of diffusion of this gas, called **radium emanation**, and by the direct weighing of an exceedingly small volume on the microbalance, its atomic or molecular weight (on the assumption that it is monatomic) was found to be 220·3. It is an inert gas belonging to the argon group. It liquefies with great sharpness between – 152° and – 154°; the liquid boils at – 65°, and solidifies at – 71°. Under the microscope the liquid is colourless and transparent, whilst the solid is opaque. The liquid glows with great brilliancy in a glass tube, with a steel-blue light which at lower temperatures changes to brilliant orange-red. Ramsay, therefore, proposed for the gas the name **niton,** Nt (Latin *nitidus* = shining). It has a characteristic spectrum, similar to that of xenon, and is distinctly soluble in water.

Production of helium from radium emanation.—Ramsay and Soddy observed that, on standing, the emanation of radium, or niton, gradually lost its characteristic spectrum, whilst the **helium** spectrum appeared. The conversion of niton into helium was definitely proved by the experiment of Rutherford and Royds already mentioned. $3 \cdot 4 \times 10^{10}$ atoms of helium are produced from 1 gm. of radium per second; the volume of emanation in equilibrium with 1 gm. of radium is 0·585 cu. mm. This emanation is continually undergoing transformation into helium and other products, and fresh emanation is constantly produced from the radium. **Radioactive equilibrium** is therefore not the same thing as ordinary chemical equilibrium.

FIG. 435.—Tracks of γ-rays.

The atomic weight of radium is 224·2; the observed density of niton is 110·6, hence the atomic weight is 221·2. The difference is 3·0, roughly the atomic weight of helium. The emanation is therefore produced together with one α-particle in the first step in the disintegration of radium: Ra (224·2) = α-particle (He = 3·97) + Nt (220·3). Two gases helium and niton are thus the first product from the solid radium. The activity of radium was found to be quite unaffected by temperature; it is the same in liquid air as at a red heat. In this respect, **radioactive changes** differ completely from ordinary chemical reactions, the velocity of which is very largely influenced by temperature.

Theory of atomic disintegration.—There is no doubt that radium is an **element.** It possesses a definite atomic weight, has a definite spectrum, and occupies a definite position in the periodic system. The experiments described above show, however, that radium is constantly changing into two gases, helium and niton. Each of these is an element in the same sense as radium. Niton, like radium, is unstable and produces helium and a solid, which is deposited on surfaces exposed to the emanation of radium. This solid is called the **active deposit,** because it in turn gives rise to other products in definite stages, each stage in the transformation being accompanied by the emission of α-rays, *i.e.*, helium atoms, or β-rays (electrons) and γ-rays. As will be seen later, there are eight changes passed through in succession from radium to the final product, which is inactive, and altogether five α-particles and four β-particles are emitted. The atomic weight of radium is 224·2, and the five α-particles have a mass of $5 \times 3{\cdot}97 = 19{\cdot}9$, hence the atomic weight of the final product will be $224{\cdot}2 - 19{\cdot}9 = 204{\cdot}3$. The atomic weight of lead is 205·55, hence it would seem probable that the final product of the disintegration of radium is **lead.** This has been confirmed.

In the above description of the properties of radium, it is assumed that the atoms of that element and those of some of the products of change break down and produce new atoms. The puzzle as to the source of the energy emitted by radium is cleared up by this hypothesis, since it comes largely from the kinetic energy of the swift and relatively massive α-particles shot from the disintegrating atoms. The idea of the **spontaneous disintegration of atoms** was put forward by Rutherford and Soddy in 1903; it follows naturally from the observed phenomena.

In radioactive changes the **transmutation of the elements,** so long but so vainly sought by the alchemists, is proceeding of its own accord. No human effort can in the minutest detail change any phase of the process: the rate at which the atoms break down is unchanged by temperature, by chemical reagents, or by any other means.

Average life.—An atom of a radioactive element is at any moment liable to explode, as it were, and give rise to other atoms and possibly free electrons. The expectation of life of the atoms is governed by a simple law, discovered by Rutherford. The fraction of the total number of atoms undergoing disintegration in unit time is constant; in other words, the activity diminishes exponentially with the time. The inverse of the fraction disintegrating per unit time is called the **average life,** of the element; it is 1·443 times the period in which half the atoms have undergone disintegration (**half-life**). Each radioactive element is characterised by its average life, which may vary from some millionths of a second, to millions of years, according as the element is very unstable, or is more stable, undergoing only slow change.

Radioactivity of uranium.—In 1900 Crookes found that if an ordinary uranium salt, the radioactivity of which had been discovered by Becquerel in 1896, is treated with ammonium carbonate, a slight residue is left in which all the photographic activity of the original salt is concentrated. The solution emits α-rays, which discharge an electroscope but do not affect a photographic plate, whilst the residue emits β- and γ-rays, which are photographically active. The precipitate was called **uranium-X**; on standing it became inactive, whilst the solution regained its activity, and yielded another specimen of uranium-X. Uranium is therefore capable of growing uranium-X.

Boltwood and Soddy found that radium is produced spontaneously from uranium, but the change is not a direct one. An intermediate element, called **ionium,** was separated by Boltwood from the mineral carnotite. The same observer also noticed that uranium in disintegration appears to give out two *α*-particles, instead of one, as is the case with most radioactive atoms emitting *α*-rays. This suggests that there are two varieties of uranium; these have been called **uranium-I** and **uranium-II.** Uranium-X also appears to pass into ionium through an intermediate element known as **uranium-X_2.** The complete **series of transformations of uranium,** which includes that of radium, of which uranium is the parent, is given in the table below. The periods of average life of the products are given above the symbols; the values of the average life are in years (*y*), days (*d*), hours (*h*), minutes (*m*), and seconds (*s*). The *α*-particle, or the helium atom minus two electrons, is denoted by **He**; the *β*-ray, or the free electron, by ϵ.

DISINTEGRATION SERIES OF URANIUM.

$$\overset{3\times10^{9}y.}{\mathrm{U_{I}}} \rightarrow \mathbf{He} + \overset{35{\cdot}5d.}{\mathrm{UX_1}} \rightarrow \epsilon + \overset{1{\cdot}65m.}{\mathrm{UX_2}} \rightarrow \epsilon + \overset{?\,3\times10^{6}y.}{\mathrm{U_{II}}} \rightarrow \mathbf{He} + \overset{10^{5}y.}{\mathrm{Io}} \rightarrow \mathbf{He} + \overset{2440y.}{\mathrm{Ra}}$$

$$\overset{2440y.}{\mathrm{Ra}} \rightarrow \mathbf{He} + \overset{5{\cdot}55d.}{\mathrm{Nt}} \rightarrow \mathbf{He} + \overset{4{\cdot}3m.}{\mathrm{RaA}} \rightarrow \mathbf{He} + \overset{38{\cdot}5m.}{\mathrm{RaB}} \rightarrow \epsilon + \overset{28{\cdot}1m.}{\mathrm{RaC}}$$

$$\overset{28{\cdot}1m.}{\mathrm{RaC}} \begin{array}{l} \nearrow (0{\cdot}003 \text{ per cent.})\ \mathbf{He} + \overset{1{\cdot}9m.}{\mathrm{RaC_2}} \rightarrow \epsilon + \mathrm{Pb}\ \text{(end-product).} \\ \searrow (99{\cdot}997 \text{ per cent.})\ \epsilon + \overset{?\,10^{-6}s.}{\mathrm{RaC_1}} \rightarrow \mathbf{He} + \overset{24y.}{\mathrm{RaD}} \rightarrow \epsilon + \overset{7{\cdot}2d.}{\mathrm{RaE}} \end{array}$$

$$\rightarrow \epsilon + \overset{196d.}{\mathrm{RaF}} \rightarrow \mathbf{He} + \mathrm{Pb}\ \text{(end-product).}$$

RaC_2 and its end-product are members of a **branch-chain.**

Radioactivity of thorium.—In 1906 Rutherford and Soddy found that thorium gives off a characteristic **emanation,** which behaves as a gas. By adding ammonia to a solution of a thorium salt they found that the filtrate from the thorium hydroxide contained a very active substance, to which they gave the name **thorium-X.** After a month's time, the thorium-X had completely lost its activity, whilst the precipitate of thorium hydroxide had recovered exactly the activity of the original thorium salt, *i.e.*, the activity which had been lost by the thorium-X. More recent research shows that Th-X is formed from Th through three intermediate products, called **mesothorium-I, mesothorium-II,** and **radiothorium.** When Th-C_1 is reached, the atoms may disintegrate further in two different ways. Thirty-five per cent. of the Th-C_1 atoms emit an *α*-particle forming Th-D, which then emits a *β*-ray, forming lead, whilst 65 per cent. of the Th-C_1 atoms emit β-rays, forming Th-C_2, which then emits an α-particle, forming lead. Although the net result is the same in both cases, viz., the emission of an α-particle and a β-ray, these changes occur in a different order, and the two final products, although having the same atomic weight, may have different internal energies and may be regarded as different atoms. No detectable rays are emitted by Ms-Th_1, so that the production of Ms-Th_2 from it is called a **rayless change.**

DISINTEGRATION SERIES OF THORIUM

$$\overset{25\times 10^{10}y.}{\mathrm{Th}} \rightarrow \mathbf{He} + \overset{9{\cdot}67y.}{\mathrm{MsTh_1}} \rightarrow \overset{8{\cdot}9h.}{\mathrm{MsTh_2}} \rightarrow \mathbf{He} + \overset{2{\cdot}75y.}{\mathrm{RdTh}} \rightarrow$$

$$\mathbf{He} + \overset{5{\cdot}25d.}{\mathrm{ThX}} \rightarrow \mathbf{He} + \overset{78s.}{\mathrm{ThEman.}}$$

$$\overset{78s.}{\mathrm{ThEman.}} \rightarrow \mathbf{He} + \overset{0{\cdot}2s.}{\mathrm{ThA}} \rightarrow \mathbf{He} + \overset{15{\cdot}4h.}{\mathrm{ThB}} \rightarrow \epsilon + \overset{87m.}{\mathrm{ThC_1}}.$$

$$\overset{87m.}{\mathrm{ThC_1}} \begin{array}{l} \nearrow (35 \text{ per cent.})\ \mathbf{He} + \overset{4{\cdot}5m.}{\mathrm{ThD}} \rightarrow \epsilon + \mathrm{Pb} \text{ (end-product).} \\ \searrow (65 \text{ per cent.})\ \epsilon + \overset{?\,10^{-11}s.}{\mathrm{ThC_2}} \rightarrow \mathbf{He} + \mathrm{Pb} \text{ (end-product).} \end{array}$$

The actinium series.—Debierne in 1899 separated from the iron group in the residues of pitchblende from which radium was prepared another active substance, which he called **actinium.** The position of this element in the radioactive series was a puzzle until Rutherford suggested that it was a branch-chain product, derived from uranium-II. Ninety-two per cent. of the U_{II} atoms emit α-particles, forming ionium, but 8 per cent. of them appear to emit α-particles, forming a different product, known as uranium-Y. This emits a β-ray, forming an element recently discovered by Soddy, called **eka-tantalum,** which gives rise to actinium by emission of an α-particle. The final product is a variety of lead.

DISINTEGRATION SERIES OF ACTINIUM.

$$\overset{?\,3\times 10^{6}y.}{\mathrm{U_{II}}} \begin{array}{l} \nearrow (92 \text{ per cent.})\ \mathbf{He} + \mathrm{Io}, \text{ etc.} \\ \searrow (8 \text{ per cent.})\ \mathbf{He} + \overset{22d.}{\mathrm{UY}} \rightarrow \epsilon + \overset{?\,10^3 \text{ to } 10^4y.}{\mathrm{EkaTa}} \rightarrow \mathbf{He} + \overset{?\,30y.}{\mathrm{Ac}} \rightarrow \end{array}$$

$$\epsilon + \overset{28{\cdot}1d.}{\mathrm{RdAc}} \rightarrow \mathbf{He} + \overset{16{\cdot}4d.}{\mathrm{AcX}}$$

$$\overset{16{\cdot}4d.}{\mathrm{AcX}} \rightarrow \mathbf{He} + \overset{5{\cdot}6s.}{\mathrm{Ac\ Eman.}} \rightarrow \mathbf{He} + \overset{0{\cdot}003s.}{\mathrm{AcA}} \rightarrow \mathbf{He} + \overset{52{\cdot}1m.}{\mathrm{AcB}} \rightarrow$$

$$\epsilon + \overset{3{\cdot}1m.}{\mathrm{AcC}} \rightarrow \mathbf{He} + \overset{6.83m.}{\mathrm{AcD}} \rightarrow \epsilon + \mathrm{Pb} \text{ (final product).}$$

It is not yet definitely decided whether UY is derived from U_I or from U_{II}. It has even been suggested that actinium is derived from a third isotope (p. 1033) of uranium, which is not a member of the uranium-radium series but a distinct primary radio-element, called **actinouranium.**

Atomic numbers.—Kaye (1909) found that a solid element, when bombarded by a sufficiently rapid stream of cathode rays, emits a characteristic X-radiation, which may be resolved into a spectrum by reflexion from a crystal, as explained on p. 1019. Moseley (1913–4) used a crystal of potassium ferrocyanide and photographed the spectra of various elements.

The elements (*e.g.*, W, Fe, Cu), or their solid compounds (*e.g.*, KCl), were used as anticathodes in an X-ray bulb, being mounted on a trolley inside the bulb so that they could be brought in succession in front of the cathode by means of a magnet outside.

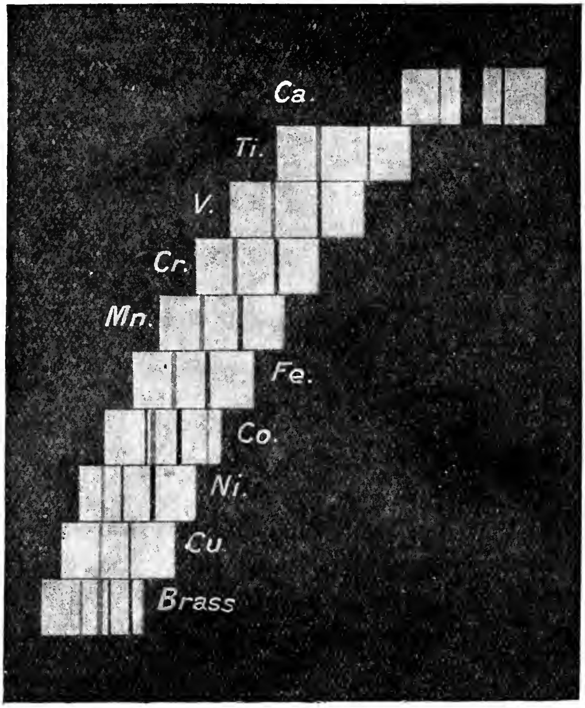


FIG. 436.—X-ray Spectra.

The spectra consisted in all cases of two main lines, the frequencies of which decreased in a regular manner as the atomic weights of the elements increased (Fig. 436). The square-roots of the frequencies of corresponding lines in the spectra of successive elements, taken in the order of their positions in the Periodic Table, when plotted against the number of the element in this table, gave

TABLE OF ATOMIC NUMBERS AND ATOMIC WEIGHTS.

I	1	Hydrogen	H	1·00					
II	2	Helium	He	3·97	III	10	Neon	Ne	20·0
	3	Lithium	Li	6·89		**11**	Sodium	Na	22·82
	4	Beryllium	Be	9·0		12	Magnesium	Mg	24·13
	5	Boron	B	10·8		**13**	Aluminium	Al	26·8
	6	Carbon	C	11·91		**14**	Silicon	Si	28·1
	7	Nitrogen	N	13·90		15	Phosphorus	P	30·79
	8	Oxygen	O	15·87		16	Sulphur	S	31·81
	9	Fluorine	F	18·9		**17**	Chlorine	Cl	35·18
IV	18	Argon	A	39·6	V	36	Krypton	Kr	82·26
	19	Potassium	K	38·79		.37	Rubidium	Rb	84·77
	20	Calcium	Ca	39·75		38	Strontium	Sr	86·93
	21	Scandium	Sc	44·7		**39**	Yttrium	Yt	88·62
	22	Titanium	Ti	47·72		**40**	Zirconium	Zr	89·9
	23	Vanadium	V	50·6		**41**	Niobium	Nb	92·4
	24	Chromium	Cr	51·6		**42**	Molybdenum	Mo	95·2
	25	Manganese	Mn	54·49		43	—	—	—
	26	Iron	Fe	55·40		**44**	Ruthenium	Ru	100·9
	27	Cobalt	Co	58·50		**45**	Rhodium	Rh	102·1
	28	Nickel	Ni	58·21		**46**	Palladium	Pd	105·9
	29	Copper	Cu	63·07		**47**	Silver	Ag	107·04
	30	Zinc	Zn	64·85		48	Cadmium	Cd	111·51
	31	Gallium	Ga	69·5		49	Indium	In	113·9
	32	Germanium	Ge	71·9		**50**	Tin	Sn	117·8
	33	Arsenic	As	74·37		**51**	Antimony	Sb	119·2
	34	Selenium	Se	78·6		**52**	Tellurium	Te	126·5
	35	Bromine	Br	79·29		**53**	Iodine	I	125·91
VI	54	Xenon	Xe	129·2		**74**	Tungsten	W	182·5
	55	Cæsium	Cs	131·76		75	—	—	—
	56	Barium	Ba	136·28		**76**	Osmium	Os	189·4
	57	Lanthanum	La	137·9		**77**	Iridium	Ir	191·6
	58	Cerium	Ce	139·15		**78**	Platinum	Pt	193·6
	59	Praseodymium	Pr	139·8		**79**	Gold	Au	195·6
	60	Neodymium	Nd	143·2		**80**	Mercury	Hg	199·0
	61	—	—	—		**81**	Thallium	Tl	202·4
	62	Samarium	Sa	149·2		**82**	Lead	Pb	205·55
	63	Europium	Eu	150·8		**83**	Bismuth	Bi	206·4
	64	Gadolinium	Gd	156·1		**84**	Polonium, or	RaF	—
	65	Terbium	Tb	157·9		85	—	—	—
	66	Dysprosium	Ds	161·2					
	67	Holmium	Ho	162·2	VII	86	Niton	Nt	220·6
	68	Erbium	Er	166·4		87	—	—	—
	69	Thulium	[1]Tm	167·2		**88**	Radium	Ra	224·2
	70	Ytterbium	Yb	172·1		89	Actinium	Ac	—
	71	Lutecium	Lu	173·6		**90**	Thorium	Th	230·31
	72	—	—	—		**91**	Uranium X_2	U-X_2	—
	73	Tantalum	Ta	180·1		**92**	Uranium	U	236·3

---

[1] Thulium has been supposed to be a mixture of two elements, Tm_1 and Tm_2, but this is not confirmed by the recent work of Urbain on the *X*-ray spectra.

practically a straight line. If ν is the frequency of the line of longer wave-length; ν_0 is a constant (Rydberg's constant); N is the number of the position of the element in the Periodic Table, or the **atomic number,** then:

$$Q = \sqrt{\nu / \tfrac{3}{4}\nu_0} = N - 1.$$

Element . . .	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic weight	40	—	48	51	52	55	56	59	58·5	63	65
Q . . .	19	—	21	22	23	24	25	26	27	28	29
N . . .	20	—	22	23	24	25	26	27	28	29	30

The order of values of Q is the same as that of the elements in the Periodic Table, although in some cases (*e.g.*, Co and Ni) the order of atomic weights is reversed. The atomic numbers of Cl and K, deduced from the equation above, are 17 and 19, leaving a gap, 18, for argon, although the latter has an atomic weight higher than that of potassium. In the table of atomic numbers given on p. 1031, the values in heavy type have been found experimentally; the total possible number of elements from hydrogen to uranium is 92, five of which still remain to be discovered. There may, of course, be other elements below hydrogen or above uranium.

The position of radio-elements in the periodic system.—The position of an element in the periodic system is fixed primarily by its atomic weight, although in one or two cases (p. 471) the chemical properties of a pair of elements lead to positions assigned in the reverse order of the atomic weights. Since the atomic weights of all the radio-elements have been determined, or (in the majority of cases) calculated from those of the parent substances by subtraction of the weight of the helium atoms expelled during the transformation, it is evident that the positions of these elements in the periodic system can be assigned.

If this is done, in conjunction with a consideration of the chemical properties of the elements, it is found that a general law holds in all cases. This states (Fajans, and Soddy, 1913) that in an α-ray change, viz., a radioactive transformation in which an α-particle is expelled from the atom, the product generated falls into a group of the periodic system *two places lower* than that to which the parent substance belongs. In a β-ray change, on the other hand, viz., one in which an electron is expelled from the atom, the product falls into a group *one place higher* than that of the parent substance.

Thus, the expulsion of an α-particle from the atom of radium, an element of the second group, leads to the formation of niton, an inactive gas of the zero group; the expulsion of a β-particle from Ra D, an element of Group IV, leads to the formation of Ra E, an element of Group V.

The whole series of radio-elements and their transformations are

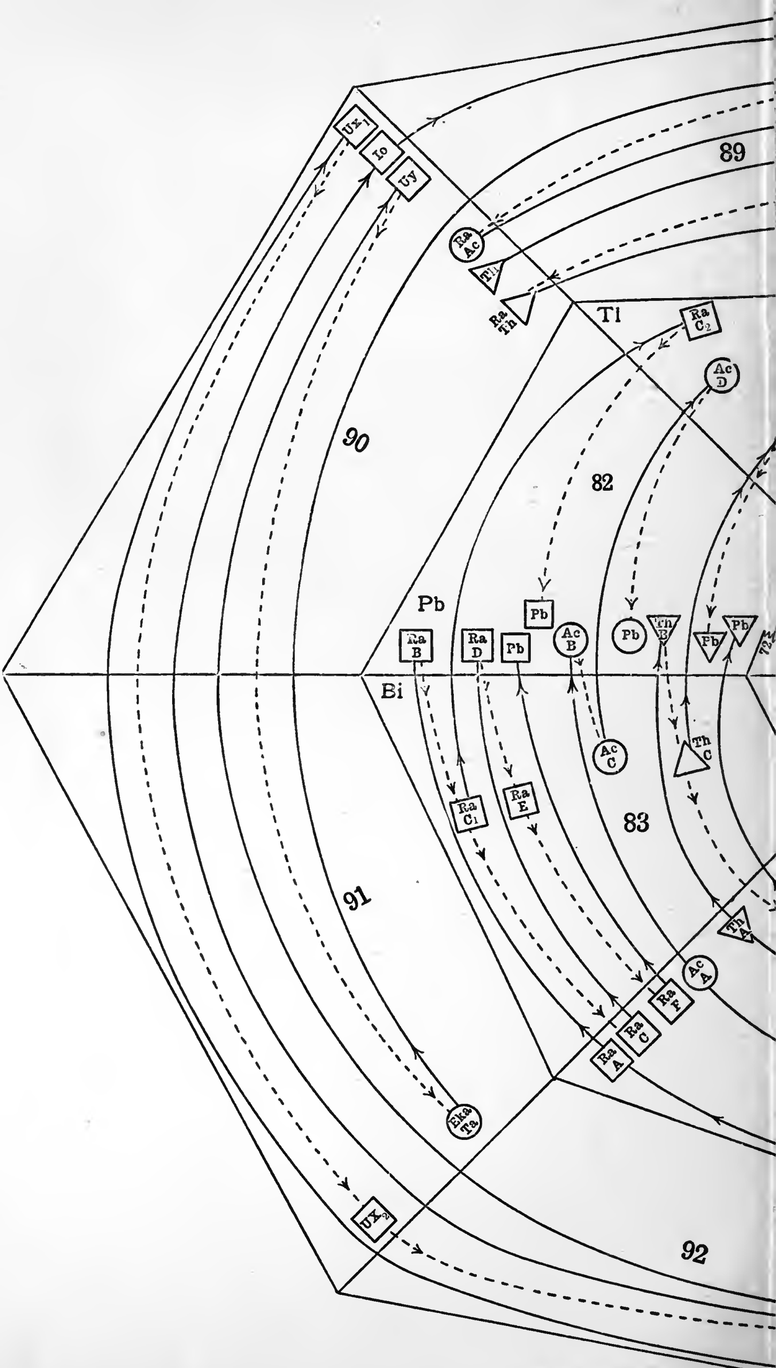
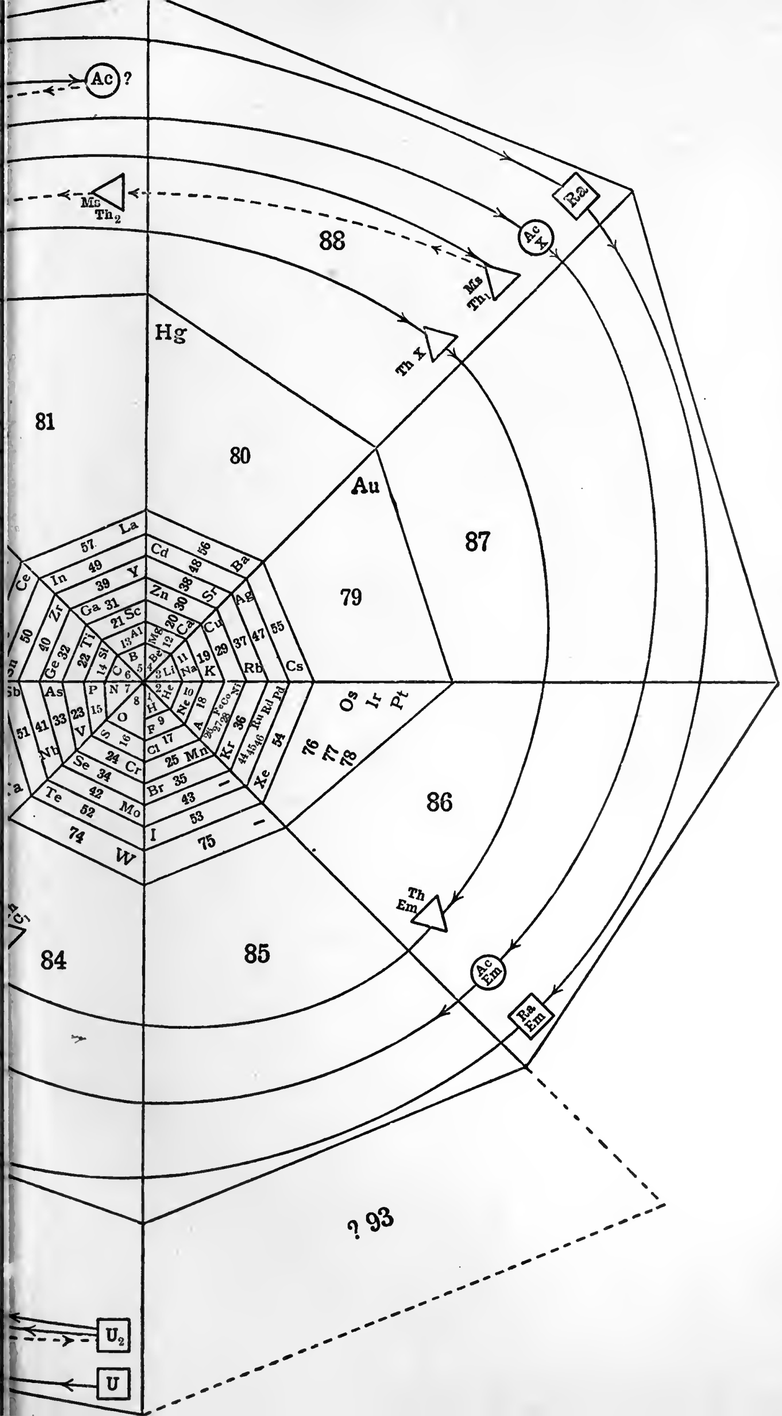


FIG. 437.—Periodic Arrangement of Elements.


Ac ?
Ms Th2
88
Ra
Ac X
Ms Th1
Th X
Hg
81
80
Au
87
79
La
57
Cd
56
Ba
In
49
Y
48
39
Zn
38
Sr
Ce
Ga 31
21 Sc
30
Ag
Zr
Ti
13 Al
Mg
20
Ca
Cu
47
55
50
40
22
Si
B
Be
12
11
19
29
37
Ge 32
14
C
5
4
3 Li
Na
K
Rb
Cs
Sn
6
Sb
As
P
N 7
2
He
10
Ni
Pd
Os
Ir
Pt
8
1
H
Ne
18
Fe Co
Rd
15
O
F 9
A
26 27 28
Ru
51
41
33
23
V
S
16
Cl 17
36
44 45 46
54
76
77
78
Nb
24 Cr
25 Mn
Kr
Se 34
Br 35
Xe
Ca
Te
42
Mo
43
52
53
I
74
W
75
86
Th Em
85
84
Ac Em
Ra Em
? 93
U2
U

shown in Fig. 437, in which their positions in the periodic table are evident. One of the most striking results appearing from this figure is that more than one element occupies the same place in the system (p. 462). The different elements occupying the same position in the table are called **isotopes**; they are inseparable one from another by chemical processes, and behave chemically as identical elements. They can be distinguished, however, by their radioactive properties, in particular by the rate of disintegration, and by the nature of the elements from which they are derived, or of the products to which they give rise. They are also differentiable by their atomic weights and by their densities, since their atomic volumes are identical. Soddy (1918) has pointed out that **two types of isotopes** exist :

1. Those of *different atomic weights,* which are products of different disintegration series, such as the varieties of lead (p. 462). These are known as **heterobaric isotopes.**

2. Those of the *same atomic weight,* produced by the successive expulsion of an α-ray and a β-ray in different orders, *i.e.*, in one case an α-ray is lost first, and then a β-ray, whilst in the second case a β-ray is first expelled, and then an α-ray. These are known as **isobaric isotopes.** Ra D and Pb from Ra C_2 are isobaric isotopes.

Elements occurring in different positions in the periodic system are called **heterotopes**; they are separable by chemical means. They may have different atomic weights, when they are called **heterobaric heterotopes**, or the same atomic weight, when they are called **isobaric heterotopes.**

It has been found that the **molecular solubilities** of compounds of isotopes are identical. Thus, the solubilities of common lead nitrate and of uranio-lead nitrate are 1·7993 and 1·7991 gm. mol. per litre, respectively. The actual weights of lead per 100 gm. of water are 37·281 and 37·130, substantially in the ratio of the atomic weights.

The **spectra** of isotopes have so far been found to be identical, both as regards the ordinary light spectra and the high frequency, or X-ray spectra. The X-ray spectra of ordinary lead and of uranio-lead were found to be identical within the error of 0·0001 Ångström unit. The infra-red spectra have been neglected, and in one case it has been thought that a minute difference has been detected in the X-ray spectra. It is also possible that isotopes may have different vapour pressures.

Fig. 437 shows that the radioactive series extends over twelve places in the periodic table, the places occupied by the halogens and the alkali-metals, viz., Groups I and VII, being entirely skipped. It is perhaps worthy of note that just these two groups contain the strongest electropositive and the strongest electronegative elements known. It is also noteworthy that, in order to preserve the relation described by Fajans, viz., the passage into the next group but one lower by the loss of an α-particle, and into the next higher group by the loss of a β-particle, the group of transitional elements, Group VIII, has to be omitted altogether. This indicates that some place should be found for these elements in the rest of the table, but so far none of the attempts to do this have been successful.

In the ten occupied places in the last two periods there are forty-three distinct types of atoms, characterised by specific radioactive properties, but these represent only ten chemically different substances. The chemical and spectroscopic characters of seven of these, viz., Tl, Pb, Bi, Nt, Ra, Th, and U, have been firmly established, and the places occupied by them accommodate all but nine of the known radio-elements.

The tendency of workers on radioactivity is to regard isotopes as different elements; since, however, they are identical in chemical properties, it has been suggested by Paneth (1916) that they should be regarded as varieties of elements, the latter being substances which cannot be simplified by chemical means. Fajans, on the other hand, adopts the view that they are different elements, and would define an **element** as a substance which cannot be separated by any chemical or physical means into simpler constituents, and cannot be recognised as a mixture of other substances (*e.g.*, a mixture of isotopes).

It is evident how deeply these discoveries reach into the fundamental conceptions of chemistry. The position has been eloquently put by Soddy, to whom so much of this fascinating work is due: "Nemesis, swift and complete, has indeed overtaken the most conservative conception in the most conservative of sciences. The first phase robbed the chemical element of its time-honoured title to be considered the ultimate unchanging constituent of matter; but since its changes were spontaneous and beyond the power of science to imitate or influence to the slightest degree, the original conception of Boyle, the practical definition of the element as the limit to which the ultimate analysis of matter had been pushed, was left almost unchanged." After pointing out that, during the last century, the atom and the element were regarded as synonymous, related as the singular to the plural, and that the atoms of any one element were considered to be identical in every respect, Soddy proceeds to say: "The second phase in the development of radioactive change has now negatived each and every one of the conceptions of last century that associated the chemical element with the atom. The atoms of the same chemical element are only chemically alike. Different chemical elements may have the same atomic mass, the same chemical element may have different atomic masses, and, most upsetting of all, the atoms of the same element may be of the same mass and yet be an unresolvable mixture of fundamentally distinct things."

The age of the earth.—Calculations by Lord Kelvin on the assumption that the earth consisted originally of a sphere of incandescent matter which has cooled by radiation into space, showed that the time required to arrive at the present condition was much shorter than the period indicated by the geological deposits and fossils. The presence of radioactive material in the earth has modified this calculation, since the heat evolved in its disintegration would make the cooling process much slower than would otherwise be the case. The source of energy in the sun may also be due partly to radioactive changes; although radium has not been detected in the solar spectrum, the presence of helium, one of the products of disintegration of radium, suggests the possibility of radioactive changes.

The structure of the atom.—The sudden and often large deflection of the a-particle at the end of its track, shown in Fig. 433, indicates that its positive charge must have approached very close to some positive charge in an atom of gas, in such a way that a large repulsive force arises between the two like charges. As the α-particle must have passed through several atoms without deflection before it is finally arrested, this positive atomic charge must be concentrated in a volume of small dimensions compared with the volume of the atom. Calculation shows that the two charges must have approached within a distance of 10^{-13} cm., *i.e.*, less than the radius of the electron and many times smaller than the radius of an atom, which is of the order of 10^{-8} cm. The atom is electrically neutral, so that in addition to the positive nucleus there must be electrons. The simplest assumption as to the structure of the atom is that it consists of a very small **positive nucleus** surrounded by one or more **electrons** revolving in circular orbits about the nucleus, the diameter of the electronic orbit being of the order of the diameter of the atom. The rest is empty space. By far the greater part of the atom is therefore space.

The electrons have a very small mass, so that the **mass of the atom** must be concentrated in the positive nucleus. The mass associated with an electric charge is inversely proportional to the radius of the charged body; the very small radius of the positive nucleus implies therefore a large mass. It is not necessary to assume that any part of the mass of the atom is not that associated with the positive charge on the nucleus and the small mass of the orbital electrons. The whole mass is then regarded as electric, and matter is looked upon as an aggregate of electric charges.

The above theory of the structure of the atom is due to Rutherford (1911). Since no positive charge has been isolated less than the mass of the **hydrogen atom**, the latter is assumed to consist of one unit positive nuclear charge, with one electron revolving around it to make the whole electrically neutral (Fig. 438). The **helium atom** would then contain a nucleus carrying four unit positive charges and two electrons. The nucleus in this case is identical with the α-particle; the positive nucleus of the hydrogen atom, or the unit positive charge, is the hydrogen ion. The series of atomic numbers suggests that successive atoms, counting from helium, have nuclei containing one additional charge for each step in atomic number. All atoms contain the unit positive charge, *i.e.*, the hydrogen ion, as the basis of the nucleus. The helium nucleus appears to be a secondary nucleus of great stability.

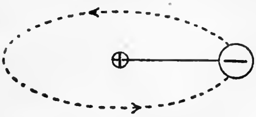


FIG. 438.—Structure of Hydrogen Atom.

In chemical changes only the orbital electrons are disturbed. The ionisation of potassium, for instance, implies a loss of one orbital electron, the nucleus remaining unchanged. The vibrations of orbital electrons, or their shift from one orbit to another, is supposed to give rise to the radiation emitted by the atom, *i.e.*, to its spectrum. It is only in radioactive changes, when α- and β-particles are emitted, that disruption of the nucleus occurs. The electrons of β-rays are assumed to come from the nucleus, so that the latter may contain negative electrons as well as positive charges. There must always be a net positive charge on the nucleus to maintain neutrality with the orbital electrons. The α-particle consists of four hydrogen nuclei plus two nuclear electrons, since it has a net positive charge of two units. The helium atom has two orbital electrons in addition.

The structure of molecules.—The views on the structure of **molecules,** apart from those in crystals studied by the Braggs, are less definite than those relating to atoms. Debije considers that in the formation of the hydrogen molecule the two orbital electrons of the atoms are displaced. The two circular currents represented by the rotating electrons attract, whilst the positive nuclei repel, each other. The orbits of the electrons approach more rapidly than the nuclei and finally coalesce. When this occurs the hydrogen molecule is produced (Fig. 439). This consists of a pair of electrons rotating in a plane at right angles to the line joining the two nuclei.

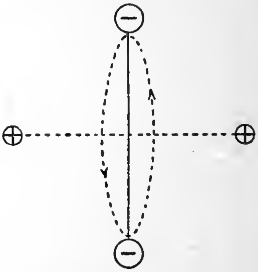


FIG. 439.—Structure of Hydrogen Molecule.

EXERCISES ON CHAPTER LI

1. How are positive rays produced? Of what do they consist?
2. Explain how X-rays have been used to study the internal structure of crystals.

3. What is the atomic number of an element ? How are these determined ?

4. Give a brief account of the phenomena of radioactivity. How was radium discovered and how is it separated from its ores ?

5. What kinds of radiations are emitted from radium ? How are they distinguished ?

6. Give a brief account of the disintegration theory of radioactivity. On what experimental evidence is it based ?

7. What are isotopes ? How is their formation explained ?

8. Describe briefly the position of the radio-elements in the Periodic System.

9. What are the modern views on the structure of the atom? On what experimental evidence are they based ? Draw diagrams indicating the structure of (*a*) the hydrogen atom, (*b*) the hydrogen molecule, (*c*) the helium atom, (*d*) the *a*-particle, (*e*) the lithium atom.

PERIODIC SYSTEM O

SERIES	GROUP 0.	GROUP I.	GROUP II	GROUP III.	GROUP IV.
	— —	R_2O RH	R_2O_2 RH_2	R_2O_3 —	R_2O_4 RH_4
1		**H 1·000**			
2	He 3·97	Li 6·89	Be 9·00	B 10·8	C 11·910
3	Ne 20·0	Na 22·82	Mg 24·13	Al 26·8	Si 28·1
4	A 39·6	K 38·79	Ca 39·75	Sc 44·7	Ti 47·72
5		Cu 63·07	Zn 64·85	Ga 69·5	Ge 71·9
6	Kr 82·26	Rb 84·77	Sr 86·93	Yt 88·62	Zr 89·9
7		Ag 107·04	Cd 111·51	In 113·9	Sn 117·8
8	Xe 129·2	Cs 131·76	Ba 136·28	La 137·9 (and 12 other elements of Rare Earths)	Ce 139·15
9		Au 195·6	Hg 199·0	Tl 202·4 Ra-C_2 Ac-D Th-D	Pb 205·55 Pb *ex* Ra-C_2 Pb *ex* Ra-F Pb *ex* Ac-D Pb *ex* Th-C_1 Pb *ex* Th-D Ra-B Ra-D Ac-B Th-B
10	Nt or Ra-Eman. 220·6 Ac-Eman Th-Eman.	—	Ra 224·2 Ac-X Ms Th_1 Th-X	Ac ? Ms Th_2	Th 230·31 U-X_1 Io U-Y Rd-Ac Rd-Th

THE ELEMENTS.

GROUP V.	GROUP VI.	GROUP VII			
R_2O_5 RH_3	R_2O_6 RH_2	R_2O_7 RH			
N 13·897	O 15·87	F 18·9			
P 30·79	S 31·81	Cl 35·18		GROUP VIII.	
V 50·6 As 74·37	Cr 51·6 Se 78·6	Mn 54·49 Br 79·29	Fe 55·40	Co 58·50	Ni 58·21
Nb 92·4 Sb 119·2	Mo 95·2 Te 126·5	— I 125·91	Ru 100·9	Rh 102·1	Pd 105·9
Ta 180·1 Bi 206·4 Ra-C_1 Ra-E Ac-C Th-C	W 182·5 Po or Ra-F Ra-A Ra-C Ac-A Th-A Th-C_1	— —	Os 189·4	Ir 191·6	Pt 193·6
Eka Ta U-X_2	U-I 236·3 U-II				

ANSWERS TO EXAMPLES

Chapter I

4. 625 : 1.

Chapter IV

4. 2·185 gm.

Chapter V

1. 45·79 c.c., 0·0654 gm. **2.** 350·8 cu. ft. **3.** 383·08 mm.
6. 53·42. **7.** 22·42. **8.** (i) 1·204 kgm. ; (ii) 83·3 per cent.
9. 0·0943 gm.

Chapter VI

4. 0·086 gm. per litre. **9.** 339·6 c.c.

Chapter VII

4. 32·64 (density of H = 0·08987 gm. per litre).
5. Ag. = 107·92, S = 16·032.

Chapter VIII

4. 139·48 gm. **5.** 157·88 litres.
6. 228 gm. ferrocyanide, 362 gm. sulphuric acid, and 19·7 gm. water.

Chapter IX

3. 578·44 gm.
4. 1·798 ; 2·326 gm. per litre ; C_2N_2 ; 2 litres of CO, 1 litre of N_2.
6. Cl_2 21·86 lit. ; CO_2 22·09 lit. ; NH_3 21·92 lit.
8. At. wts. Cl = 221·6 ; H = 6·3 ; Mol. vols. = 140 lit.
10. At. wt. 236·4. XCl_4. **13.** $\Delta = 82{\cdot}6$; $\gamma = 0{\cdot}5375$.
14. 27·818.

Chapter X

9. (*a*) 5·484 litres, (*b*) 8·954 litres.
10. 24·45 c.c. at S.T.P. ; O_2 = 47·24 per cent., N_2 = 52·76 per cent. by vol.

Chapter XI

5. 3·79 c.c.

Chapter XII

3. 0·026 lb.

Chapter XIII

2. 30·2 gm. Cl_2 ; 5·03 litres.

Chapter XV

8. 1 : 0·586.

Chapter XVI

2. 458 ampere hours.
7. 0·0853 gm.
10. 93·8 c.c. ; 0·0902 gm.

Chapter XVII

5. 260·7. Probably undissociated.
6. 364.
7. 88·3 per cent. ; 87·4.
10. 1757 ; $(H_2WO_4)_7$.

Chapter XVIII

6. 7·5 c.c.

Chapter XIX

5. 29·53 gm.

Chapter XXI

9. Nil ; 15 c.c. of O_2.

Chapter XXIII

1. Se = 78·63.
2. Al = 26·89.
5. Sp. heat of S = 0·163.
6. 0·53.
11. Isomorphous mixture 1·44 $FeCO_3 + MnCO_3$; or (Fe, Mn) CO_3.

Chapter XXVIII

6. 10·5 c.c. NH_3, 9·5 c.c. N_2.

Chapter XXXII

8. Mol. wt. = 77·5, gas is AsH_3.

Chapter XXXIII

15. 12·5 H_2, 7·5 CH_4, 80 N_2 by vol.
16. CH_4 35·8 c.c., C_2H_6 10·4 c.c., H_2 7·3 c.c.

Chapter XXXV

7. 10·94.

Chapter XLII

4. 1·0186 × 96,000 × 2 = 195,580 joules = 46,710 gm. cal.
6. 12,343 gm. cal. (Heat of formation in solution 13,200 gm. cal.)

Chapter L

5. 0·2605 gm.

INDEX

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INTERNATIONAL ATOMIC WEIGHTS (1921).

ment.	Symbol.	Atomic weight. H = 1	O = 16	Element.	Symbol.	Atomic weight. H = 1	O = 16
minium ...	Al	26·8	27·1	Neodymium...	Nd	143·2	144·3
imony ...	Sb	119·2	120·2	Neon	Ne	20·0	20·2
on	A	39·6	39·9	Nickel	Ni	58·21	58·68
enic	As	74·37	74·96	Niobium	Nb	92·4	93·1
ium	Ba	136·28	137·37	Niton	Nt	220·6	222·4
yllium......	Be	9·0	9·1	Nitrogen	N	13·897	14·008
muth	Bi	206·4	208·0	Osmium	Os	189·4	190·9
on	B	10·8	10·9	Oxygen.........	O	15·87	16·00
mine	Br	79·29	79·92	Palladium ...	Pd	105·9	106·7
lmium ...	Cd	111·51	112·40	Phosphorus	P	30·79	31·04
sium	Cs	131·76	132·81	Platinum	Pt	193·6	195·2
cium	Ca	39·75	40·07	Potassium ...	K	38·79	39·10
bon	C	11·910	12·005	Praseodymium	Pr	139·8	140·9
ium	Ce	139·15	140·25	Radium	Ra	224·2	226·0
orine	Cl	35·18	35·46	Rhodium	Rh	102·1	102·9
omium ...	Cr	51·6	52·0	Rubidium ...	Rb	84·77	85·45
balt	Co	58·50	58·97	Ruthenium ...	Ru	100·9	101·7
pper	Cu	63·07	63·57	Samarium ...	Sa	149·2	150·4
sprosium ...	Dy	161·2	162·5	Scandium ...	Sc	44·7	45·1
bium.........	Er	166·4	167·7	Selenium	Se	78·6	79·2
ropium ...	Eu	150·8	152·0	Silicon	Si	28·1	28·3
orine	F	18·9	19·0	Silver	Ag	107·04	107·88
dolinium ...	Gd	156·1	157·3	Sodium	Na	22·82	23·00
llium	Ga	69·5	70·1	Strontium ...	Sr	86·93	87·63
rmanium ...	Ge	71·9	72·5	Sulphur	S	31·81	32·06
d	Au	195·6	197·2	Tantalum ...	Ta	180·1	181·5
ium	He	3·97	4·00	Tellurium ...	Te	126·5	127·5
mium......	Ho	162·2	163·5	Terbium	Tb	157·9	159·2
drogen......	H	1·000	1·008	Thallium	Tl	202·4	204·0
ium	In	113·9	114·8	Thorium	Th	230·31	232·15
ine	I	125·91	126·92	Thulium	Tm	167·2	168·5
ium.........	Ir	191·6	193·1	Tin	Sn	117·8	118·7
n	Fe	55·40	55·84	Titanium	Ti	47·72	48·1
pton	Kr	82·26	82·92	Tungsten	W	182·5	184·0
thanum ...	La	137·9	139·0	Uranium	U	236·3	238·2
d	Pb	205·55	207·20	Vanadium ...	V	50·6	51·0
ium	Li	6·89	6·94	Xenon	Xe	129·2	130·2
ecium	Lu	173·6	175·0	Ytterbium ...	Yb	172·1	173·5
gnesium ...	Mg	24·13	24·32	Yttrium	Yt	88·62	89·33
nganese ...	Mn	54·49	54·93	Zinc	Zn	64·85	65·37
rcury	Hg	199·0	200·6	Zirconium ...	Zr	89·9	90·6
ybdenum	Mo	95·2	96·0				