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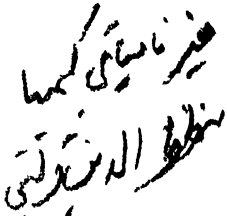

A TEXT-BOOK OF INORGANIC CHEMISTRY

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A TEXT-BOOK OF INORGANIC CHEMISTRY

FOR UNIVERSITY STUDENTS

BY

J. R. PARTINGTON, M.B.E., D.Sc.

PROFESSOR OF CHEMISTRY AT EAST LONDON COLLEGE, UNIVERSITY OF LONDON, LATELY FELLOW OF MANCHESTER UNIVERSITY

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PREFACE

THE necessity for a fourth edition of the present work so soon after the appearance of the third, in which the whole text had been closely revised, is due to the rapid advances in some branches of the subject made in the interval. The main alterations consist in the incorporation in Chapter XXV of the section on Werner's theory, with some changes and amplification of the treatment to bring it into line with modern views ; the deletion of some material in Chapter XXV which has become obsolete ; an account of the recently discovered isotopes of hydrogen and some other elements ; a general discussion of the hydrides of the elements ; the revision of the section on active nitrogen ; a table of the electronic structures of the rare-earth elements, and the inclusion in the text of a number of electronic formulae of compounds, particularly of the oxygen compounds of sulphur, nitrogen and phosphorus.

The modern theory of atomic structure has, from the first edition, been dealt with in greater detail than is usual in books of similar size and scope, and the present edition is no less complete in this respect. Very recent investigation of the structure of atomic nuclei will probably before long considerably amplify and modify present views on atomic structure, and the student who wishes to ascertain the current state of this investigation must follow the periodical literature. The table of radioactive constants, issued by International authority, has been omitted, since recently determined values are in some cases not in satisfactory agreement with one another.

The accounts of the modern theory of electrolytes and of crystal structure, included in the third edition, are also more detailed than is usual in text-books, so that the theoretical parts of the book are fully adequate to meet the needs of modern teaching. Emphasis is also laid on modern industrial processes, both in the case of non-metals and of metals. The questions and exercises have also been revised and several questions set in recent examinations added. The main features and plan of the book, which seem to have met with approval, are retained

The text-book is intended for students who have completed an introductory course, although the treatment is elementary. In those parts which are more directly of interest to advanced students the description is more concise, whilst in the elementary parts more explanatory detail is given, so that both types of student will find their needs to be met. The book will be suitable for students preparing for the Intermediate and Final B Sc. of Universities, and will serve as a reference book for higher forms in schools.

Original sources have been largely employed, and always when there was any obscurity in the large works of reference or special monographs otherwise used. In a number of cases where the appearance or reactions of a substance have been described in different ways in the literature, the actual material has been before the author and special experiments have been made in some cases to decide between conflicting statements. The physical properties and other numerical data have been carefully selected from modern researches, and several of the figures have been revised in the present edition. The tables of isotopes and of atomic weights have been omitted, since their contents are subject to frequent revision.

In the passage of the work through the press the author had valuable help from Sir Richard Gregory, and Mr. A. J. V. Gale most materially assisted in the proof-reading.

J. R. PARTINGTON

LONDON, *September*, 1933

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INORGANIC CHEMISTRY FOR UNIVERSITY STUDENTS

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 bodies having the same physical state, however, may be distinguished : coal, sugar, and salt are different solids ; water and paraffin oil are different liquids ; 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.

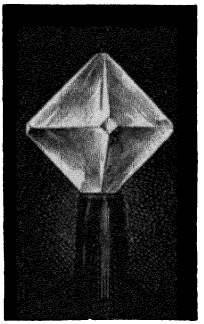


FIG. 1.—Alum Crystal.

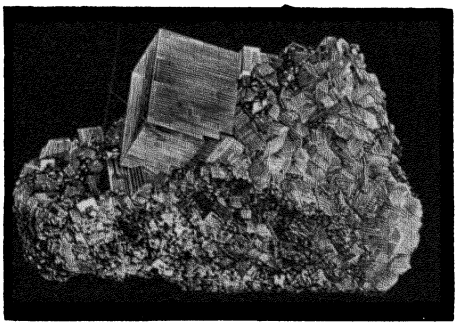


FIG. 2.—Rock-salt Crystals.

A solid sometimes has a characteristic **colour**, which enables us to pick it out from the others :

Blue vitriol : blue.
Nickel sulphate : bright green.
Potassium dichromate : bright red.
Chrome alum : dark purple.

Solids often occur in pieces with definite shapes, called **crystals**, bounded by plane faces meeting in sharp edges. When the colour is not characteristic we can often distinguish the material by its crystalline form :

Alum : octahedra (Fig. 1). **Rock salt** : cubes (Fig. 2).

Another distinguishing property of solids is **density**. **Lead nitrate**, although crystallising in the same form as alum, is much heavier. Powders of the same colour may often be distinguished by their different densities.

Solids in which the crystalline form is absent are said to be **amorphous**. 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** (Fig. 3).

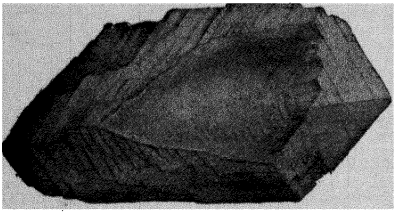


FIG. 3.—Calcite.

Showing conchoidal and crystalline fracture in the same material. (*After Miers.*)

A third method of distinguishing between solids is by the **solubility** in liquids. When finely powdered lead nitrate and barium sulphate, both heavy, white powders, are separately stirred up with hot water, 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 336°,* potassium chlorate at 357°, " hypo " at 48°, and rock salt at 801°. Barium sulphate melts only at about 1580°, whilst charcoal has probably never been fused.

Different kinds of liquids.—Liquids differ in colour, density, and **boiling point**. Some have characteristic odours. The **freezing point** of a pure liquid is usually the same as the melting point of the solid obtained from it by cooling. Some liquids flow less readily than others (*e.g.* treacle and water), or have greater **viscosity**. Water, alcohol, ether, sulphuric acid, bromine and mercury are typically different liquids.

Different kinds of gases.—The existence of different kinds of **gases** was not clearly recognised until about 1765–75, when Cavendish and Priestley showed that there were several gases differing from atmospheric air.

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

* Temperatures throughout are in degrees Centigrade.

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 flame

EXPT 4 —A jar of carbon dioxide is held over a beaker counterpoised on a balance, and slowly inverted so as to pour the gas into the beaker · 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.

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

Gases, therefore, differ in density, colour, combustibility, capacity for supporting combustion, and action on lime water.

Pure substances.—Crystals of copper sulphate differ in size, often in shape, yet all pieces of this material are composed of the same **pure substance** ; in so far as composition is concerned no account is taken of accidental circumstances such as size or shape. The two kinds of phosphorus, white and red, differ entirely in appearance and properties. Although they 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 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 there may be difficulty in defining the properties of bodies, with the view of placing them in groups of substances A piece of granite has different properties in different parts, and 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 closer study.

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**. 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**. A piece of granite is an aggregate of three different minerals. One is pink or grey, 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 third is in the form of thin grey, or black, plates, which can be split by a knife into very thin leaves ; it is **mica**.

Since the constituents of aggregates such as granite are separable by mechanical means, heterogeneous bodies are often called **mechanical mixtures**. The separate parts of a heterogeneous body are 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.

The parts of a heterogeneous body are not always so sharply differentiated as those in granite. Quartz crystals often exhibit brown colouring in different parts (" smoky quartz "), and the intensity of the colour, due to impurities, may shade off from one part of the crystal to another. Although widely-separated parts of the crystal appear quite different, and thus the whole crystal is heterogeneous, it is difficult to fix any position where definite colour change occurs

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

EXPT. 5.—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, but when a beam of light from a lantern is passed through the water, before and after adding the mastic, it will be found that little light can be seen passing through the clear water, but that water to which mastic has been added shows the path of the light as a bright, cloudy beam, called a **Tyndall cone** (Fig. 4). The same effect appears in a ray of sunlight passing through dusty air; particles of dust may be seen floating about in the beam.

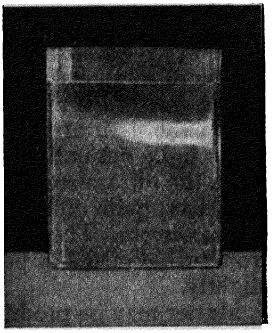


FIG. 4.—Tyndall Cone, due to the scattering of a beam of light entering at the side, by fine particles suspended in a liquid.

An instrument making use of this principle, the **ultramicroscope,** consists (Fig. 5) of a microscope with the object-glass dipping into the liquid to be examined, contained in a small glass cell. A powerful beam of light is brought to a focus in the liquid, by means of a lens. The presence of suspended particles in the liquid is 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 $0{\cdot}15\mu$ (1 *micron* $= 1\mu = 0{\cdot}001$ mm.), the ultramicroscope reveals particles down to 5×10^{-7} cm., or $5m\mu$ (1 *millimicron* $= 1m\mu = 10^{-6}$ mm.) or about one-hundredth the wavelength 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.

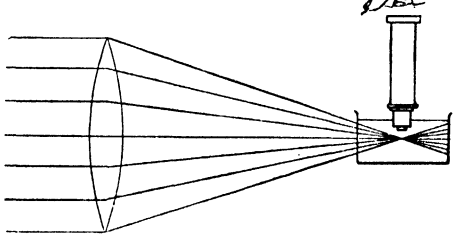


FIG. 5.—Diagram of ultramicroscope.

By the action of phosphorus on gold chloride solution, ruby-red, apparently clear, solutions are obtained, which, under the ultramicroscope, exhibit particles about $5m\mu$ in diameter. Suspensions of this kind, containing ultramicroscopic particles which do not settle out on standing and pass through filter paper, are called **colloidal solutions.** Still smaller particles of gold, not visible with the ultramicroscope, can act as nuclei, or centres of condensation, for the production of ultramicroscopic particles; the diameter of these nuclei has been estimated

at 10^{-7} cm. Zsigmondy, the inventor of the ultramicroscope, distinguished three kinds of small particles: **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).

If a few drops of eosin solution (red ink) be added to a trough of water, the path of a beam of light is rendered visible by a beautiful green light, not unlike the haze obtained with the mastic, but coloured. With the ultramicroscope, however, no particles can be detected, and the effect, quite different from that shown by turbid liquids, is known as **fluorescence**. The two effects are distinguished by the fact that light from turbid media is polarised, whilst fluorescent light is not, or only slightly.

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

Atoms.—Smaller still than the colloidal particles are the **atoms** of matter, which have diameters of the order of 10^{-8} cm. These are not seen even by the ultramicroscope, but are brought into evidence when X-rays are used instead of ordinary light. The 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, although invisible, is similar to the colours seen with visible light falling on thin soap-films The effect indicates that crystals are composed of layers of atoms, separated by distances of the order of 10^{-8} cm.

There are particles still smaller than atoms The lightest atom, that of hydrogen, consists of a positively charged nucleus, called a **proton**, having a mass nearly equal to that of the atom, and a negatively charged particle, called an **electron**, with a much smaller mass, about 1/1845 that of the hydrogen atom, situated at a distance of about 10^{-8} cm. from the proton, and probably revolving around it Both the proton and the electron are very much smaller than the atom, their diameters being of the order of 10^{-13} cm (J J Thomson; Rutherford; Bohr). Electrons and protons appear to be associated with some kind of wave-structure, the length of the "material waves" being given by $\lambda = h/mv$, where h is Planck's quantum constant (see p 385), $6{\cdot}55 \times 10^{-27}$, m is the mass and v the velocity of the particle in C G.S. units (de Broglie, Schrödinger) For fast electrons, λ is about 10^{-7} cm, so that streams of such electrons are reflected from crystals somewhat like X-rays (Davisson and Germer, G P Thomson) A similar effect is observed with protons, or nuclei of hydrogen atoms (Dempster, 1930).

All atoms are supposed to be composed of nuclei, containing protons and electrons, with a net positive charge called the **atomic number**, and

a number of outer electrons sufficient to render the whole electrically neutral (Rutherford ; Moseley , Aston)

All kinds of matter are ultimately 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 different ways.

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

(2) By differences of **density**. The powder is stirred with an inert liquid, the density of which lies between that of one of the solids and those of the others If powdered granite is shaken with a mixture of density 2·6, composed of the liquids benzene, density 0·879, and methylene iodide, density 3·33, the felspar (density 2·57) will float, whilst the mica (density 2·85) and quartz (density 2·65) 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** ; a mixture of red lead and washed and dried flowers of sulphur is dusted through muslin on to an ebonite plate rubbed with flannel: the positively charged red lead adheres to the negatively charged plate, whilst the sulphur, with the same charge as the plate, does not adhere. The plate is now tapped gently on a sheet of paper ; the sulphur with 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**) ; when 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 ; when a mixture of iron filings and sulphur is shaken with carbon disulphide the sulphur dissolves ; the solution may be decanted from the iron, which is insoluble, poured into a dish, and the solvent allowed to evaporate, when fine crystals of sulphur are left (Fig. 6).

(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** ; when a mixture of sand and iodine is heated in a test-tube, the iodine forms a beautiful violet vapour, which condenses

on the cool tube as a black crystalline **sublimate**, whilst the sand is left in the bottom of the tube.

The magnetic method separates 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 passing over a magnetic roller (Fig. 7), and falls off. The tinstone falls undeflected, but the wolfram is pulled towards the magnet, and forms a separate heap. The process is called **electromagnetic separation.**

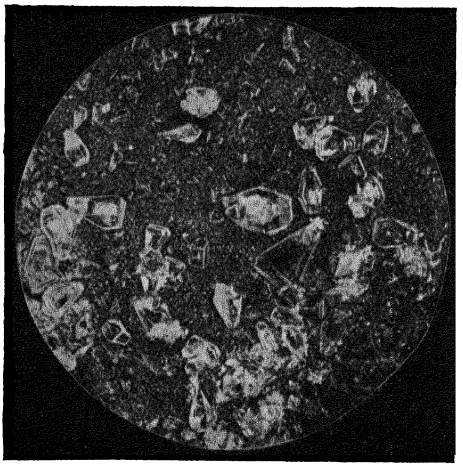


FIG. 6.—Sulphur crystals.

Separation by surface tension is used in the **flotation process** for separating minerals, such as zinc blende, not easily wetted by water, from galena (an ore of lead), which is. The crushed

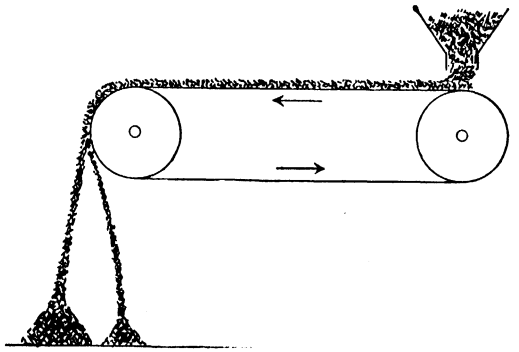


FIG. 7.—Electromagnetic separation (diagrammatic).

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**

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

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

The rates of deposition of particles of sulphur ($d = 2{\cdot}06$) in water ($d = 1{\cdot}00$, $\eta = 11\ 4 \times 10^{-3}$ at 15°), the diameters of the sulphur particles being 0 1 cm , and 0 0001 cm , calculated from Stokes's formula, are 50 cm per sec , and 0 00005 cm per sec , respectively The fine particles remain almost permanently in suspension, forming a colloidal solution

Particles of different sizes mixed together may be separated by **fractional sedimentation** ; the powder is stirred with water, and the time of settling divided into a number of intervals. A series of powders increasing in fineness is thus obtained, and the process may be repeated with each.

(2) By **centrifugal force.**—If a glass tube is filled with a fine suspension and is placed in one of the metal-containing tubes of a centrifuge (Fig. 8), a similar tube of water being put in the opposite side as a counterpoise, the powder is separated to the bottom of the tube on working the machine.

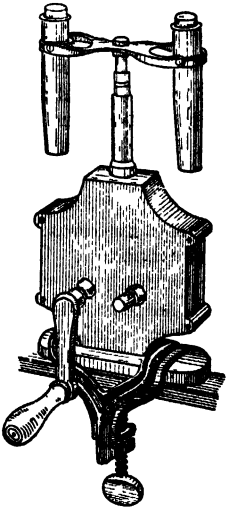


FIG. 8.—Centrifuge.

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

EXPT. 6.—A **colloidal solution** of arsenic sulphide is made by pouring a solution of arsenic trioxide in water into sulphuretted hydrogen water, and driving out the excess of the latter gas by a stream of washed hydrogen. About 50 c.c. of the yellow solution, with 5 gm. of urea

dissolved in it to make it denser than water, are carefully run by a pipette into the lower part of a U-tube half-filled with distilled water. Platinum electrodes are placed in each arm of the tube, and connected with the D C mains The level of arsenic sulphide, marked by paper rings, falls on one side of the U-tube, and rises on the other (Fig 9) The existence of suspended particles in the colloidal solution may be seen by a beam of light, as in Expt. 5

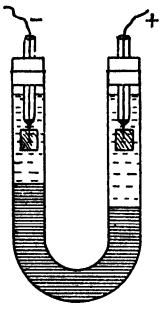


FIG. 9.—Cataphoresis.

(4) If a few drops of sulphuric acid are added to colloidal 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 arsenic sulphide with it. This is an application of the **flotation process** : arsenic sulphide adheres more strongly to oil than to water.

(5) The commonest method of separating solids from liquids is by **filtration.** Hot solutions filter more rapidly than cold ones, since the viscosity of the liquid is reduced by raising the temperature.

The rate of filtration is also increased by increasing the difference of pressure between the two ends of the capillary pores of the filter (**filtration under reduced pressure**).

The separation of liquids from liquids.—Chloroform and water when shaken together in a **separating funnel** (Fig. 10), and allowed to stand, separate into two layers with the heavy chloroform at the bottom. This can be run off through the tap, leaving the water in the funnel.

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

Emulsions can often be separated in the centrifuge, or, if one liquid is soluble in a third, whilst the second is not, by shaking with the third liquid. If ether is shaken with an emulsion of paraffin oil and water, the ether dissolves the paraffin, and the solution floats to the surface.

FIG. 10.—Separating funnel.

The separation of gases from liquids and solids.—Gases mix with each other in all proportions, so that heterogeneous systems can be obtained only transiently, when a light gas is stratified on a heavier one. They soon mix by **diffusion.**

EXPT. 7.—Pass carbon dioxide into a large jar, so that the latter is

partially filled with the gas (Fig 11). Blow a soap bubble * and allow it to fall into the jar It is arrested on reaching the carbon dioxide, and remains suspended. A lighted taper lowered into the jar is extinguished at the level of the bubble

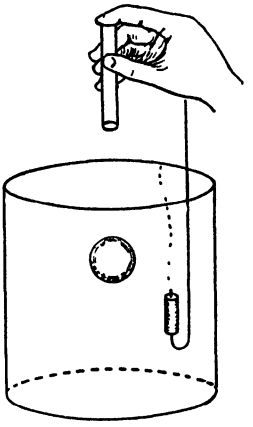


Fig 11 —Experiment illustrating stratification of gases.

A suspension of minute bubbles of gas in a liquid is a **froth** or **foam**, and 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 coalesce into larger drops.

Aitken showed that mists are produced by condensation on minute solid particles of dust or (more probably) salt (*motes*) in the air ; if these are partly removed by filtering through cotton-wool, on cooling condensation occurs on the remaining nuclei, producing rain-like drops. If all the nuclei are removed by allowing the air to stand in a vessel with wetted sides, condensation does not occur until the air is cooled much below the normal temperature of mist-formation. C. T. R. Wilson found that electrically charged nuclei, **gaseous ions**, produced even in dust-free air by electric sparks, or exposure to X-rays, can also act as condensation centres, and may also be filtered out by cotton-wool.

A suspension of fine particles of solid in a gas is a **smoke** or **fume.** Coal smoke consists mainly of small particles of carbon, which aggregate to form soot. Smoke from the glowing tip of a cigarette, also consisting of small particles of carbon, appears blue, because the particles are very fine, with diameters of the order of a wave-length of light. Smoke rising vertically from a chimney in clear dry air also appears blue, but smoke some distance from the end of a 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.

* **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.

The particles in fogs and smokes may be 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 may be precipitated, as was shown by Sir Oliver Lodge in 1883. This method of fume dissipation is applied to the precipitation of fumes from smelting furnaces, blast-furnaces, cement-furnaces, etc.

EXPT 8.—Fill a bell-jar with fumes of ammonium chloride by passing air through two flasks containing strong hydrochloric acid and ammonia solution, respectively (Fig. 12) Place the bell-jar on a metal plate

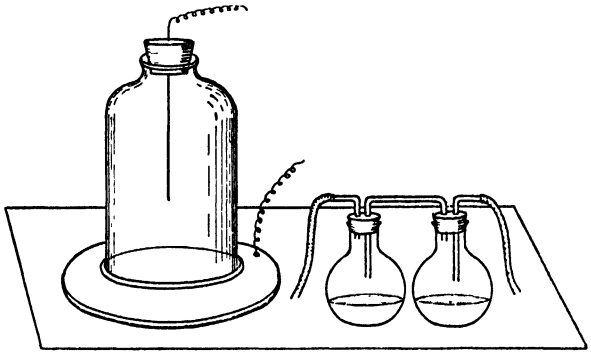


FIG. 12.—Electrical fume precipitation.

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

The **Lodge-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.

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.

CHAPTER II

ELEMENTS, COMPOUNDS, AND SOLUTIONS

Chemical changes.—Bodies often undergo radical changes under certain conditions. Bright copper becomes dull, and ultimately covered with a green crust, and iron rusts away completely to a brown powder when exposed to moist air A candle burns away, and apparently disappears.

In other cases the properties of the materials are only slightly, and temporarily, modified water on cooling freezes to ice, but the ice melts, and is reconverted into water, on warming, a bar of iron heated to redness is only slightly altered and, apart from a little scale on the surface, is recovered without change on cooling

EXPT 1.—Heat a piece of platinum wire in a Bunsen flame The wire becomes red-hot, but on cooling is quite unchanged Repeat the experiment with a piece of magnesium ribbon This takes fire and burns with a brilliant white flame, producing a white ash

Material changes may therefore be divided 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. 2.—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 3.—Pour into separate test-glasses a little of the following solutions. potassium ferrocyanide, 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. 4.—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 5.—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 to redness 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, 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 6.—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 mass.—The **mass** of a body, as determined by comparing its **weight** with that of standards by means of the ordinary balance, is generally regarded as a fixed property of the body, and a measure of the **quantity of matter** contained in it.

Empedocles, 490–430 B.C., 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 similar to the statement of Lavoisier (1743–1794 A.D.), made 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, was founded upon experiment, and is called the **law of conservation of mass,** or the **law of indestructibility of matter.** Each aspect of it is now believed to be only approximate.

The early chemists ignored changes of weight occurring in chemical processes, as removed from purely chemical studies, and beneath notice. 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]." Black put down loss of weight in a chemical change to the escape of invisible material, thus recognising implicitly the principle stated later by Lavoisier. Black's experiment is an example of chemical change in which an apparent destruction of matter is due to the escape of a gas Since the existence of gases was not clearly recognised until the eighteenth century, a belief in the actual destruction of matter survived until that period

Experiments on the conservation of mass.—When a candle burns it is apparently completely destroyed. It can be shown by experiment that this is not the case.

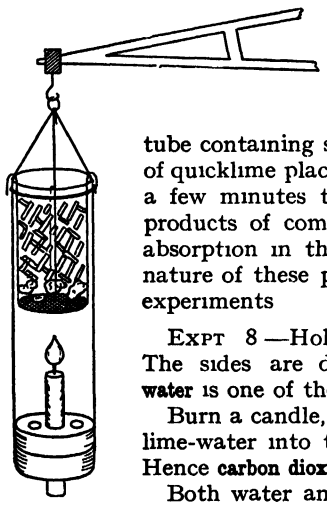


FIG. 13 — Burning of a candle.

EXPT 7 —A small candle is allowed to burn inside a counterpoised glass tube containing sticks of caustic soda, supported on pieces of quicklime placed on the top of wire gauze (Fig 13) In a few minutes there is an increase of weight, since the products of combustion are prevented from escaping by absorption in the quicklime and the caustic soda The nature of these products may be found by the following experiments

EXPT 8 —Hold a dry beaker over a burning candle The sides are dimmed by deposited moisture. Hence **water** is one of the products of combustion of a candle.

Burn a candle, supported by a wire, in a gas jar Pour 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. 7 renders it probable that the **air** has taken part in the combustion, and that the products, which are absorbed by the quicklime and the caustic soda, contain part of the air. If this is the case air must possess

weight. This is proved by the following experiment of Otto von Guericke, the inventor of the air-pump (1654).

EXPT. 9 —Exhaust by an air-pump, and counterpoise on the balance a 2-litre globe, fitted with a stopcock (Fig 14) Open the stopcock, notice the hissing noise of the air rushing into the globe, replace the globe on the balance, and notice that it has increased in weight

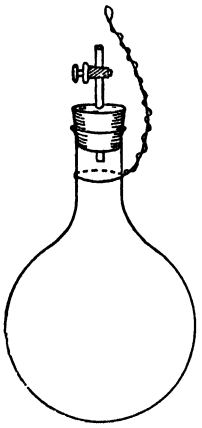


FIG 14 —Flask for weighing air

In order to test the truth of Lavoisier's principle the chemical change (or **chemical reaction**) must be instituted in a closed space, so that no material used can escape.

EXPT 10 —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 rubber stopper Weigh the flask Warm over a flame the spot where the phosphorus lies until the latter ignites When the combustion is finished, allow the flask to cool, and reweigh The weight is unchanged

EXPT 11 —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 15), 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

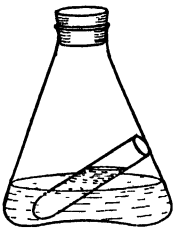


FIG 15.—Experiment on the law of conservation of matter

Landolt's experiments.—In 1900 Heydweiller stated that small losses of weight occurred when certain chemical reactions were carried out in sealed vessels 80 gm. of copper sulphate, dissolved in 130 c c. of water, were decomposed with 15 gm. of metallic iron, with a loss of weight of 0·217 mgm. H Landolt in 1893 began a series of experiments, completed in 1908, with the object of determining whether the losses noticed were real, or due to some error of experiment.

In the separate legs of a Jena glass U-tube (Fig. 16) he sealed 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 the balance and inverted, and the process repeated

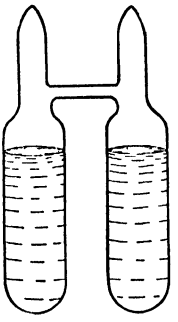


FIG 16 —Landolt's experiment

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 mass may be considered to be exact.

According to the Theory of Relativity, the absolute energy, E, of a mass m is $E = mc^2$, where c is the velocity of light A chemical change attended by a loss of energy ΔE will then give rise to a loss of mass $\Delta m = \Delta E/c^2$ Since c is very large this loss will be quite negligible in ordinary reactions to produce a loss of 1 mgm in Expt 10 would require the combustion of $3\frac{3}{4}$ tons of phosphorus. In the formation of atoms from the positive and negative charges believed to constitute them (see Chap I.) the changes of mass would be appreciable, since very large energy changes would occur. In forming an atom of helium, of relative mass 4, from four hydrogen atoms, of relative mass $4 \times 1{\cdot}008$, the mass 0·032 is lost and a very large evolution of energy occurs. Very penetrating radiations, believed to originate in the formation of atoms from positive and negative charges in the universe, have been detected as the so-called **cosmic rays.**

Elements and compounds.—A homogeneous material may undergo chemical changes in one of three ways, according to its composition. The substance may **increase in weight** in all the changes which it undergoes; it may give other substances, each of smaller weight than the original substance, or, as is said, may **decompose**; or, finally, its weight may remain the same. The third case (**isomeric** or **allotropic change**) is considered later.

EXPT. 12.—Heat 0·5 gm. of magnesium ribbon in a weighed, loosely closed, porcelain crucible, with a small flame, till combustion ceases (Fig. 17). Then heat strongly for ten minutes with the lid off, cool, and reweigh. Repeat the heating until the weight is constant. There is an *increase in weight* of a little over 0·3 gm.

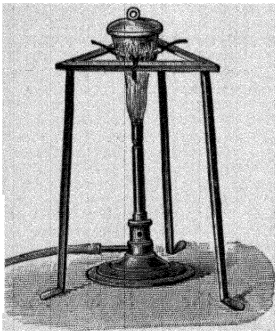


FIG. 17.—Heating magnesium in air.

EXPT. 13.—Heat 2·16 gm. of red oxide of mercury in a weighed, hard glass tube, with a glass delivery tube leading to a pneumatic trough in which is inverted a measuring cylinder full of water (Fig. 18). 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 tube. When 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. The *loss in weight* of the tube should amount to 0·16 gm. The volume of gas collected will be about 118 c.c. A glowing chip of wood is rekindled in the gas, indicating that the latter is **oxygen.**

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, it is said to be a **Compound.** If it always yields substances of greater weight, indicating that, in all reactions in which it takes part, union occurs with other substances, and never decomposition, the substance is called an **Element.** Magnesium is an element. A substance which does not alter in weight after undergoing *chemical* change may be either an element or a compound.

At this point we meet again a difficulty encountered in Chapter I, viz., that in some cases a homogeneous material has a continuous range of compositions. Solutions of common salt in water at 0° 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, we find that it always has the same composition, containing 8 gm. of oxygen to 100 gm. of mercury.

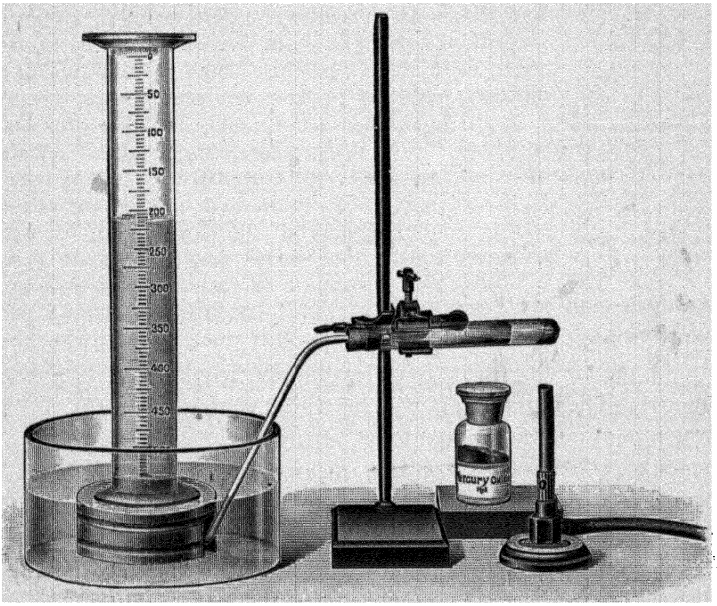


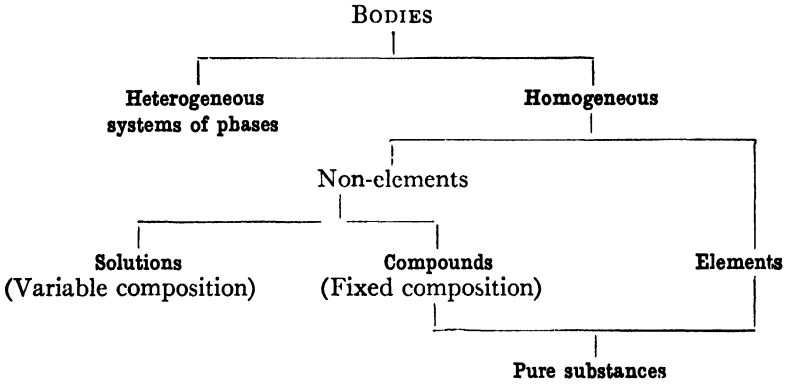
FIG. 18.—Decomposition of oxide of mercury by heat.

We therefore divide into two classes all 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.

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

The homogeneous liquids formed from salt and water 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, 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 14.—Metallic tin may be converted into oxide of tin in three different ways

(*a*) One gm. of tin is weighed into a counterpoised Rose's crucible (Fig. 19), 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 tin 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 excess of acid is evaporated off on a sand-bath, and the dry material heated for a few minutes over a Bunsen flame The dish is cooled and weighed The residue is oxide of tin

(*c*) One gm. of tin is weighed into a conical flask and dissolved in hydrochloric acid by warming 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, the filter paper and precipitate ignited in a weighed porcelain crucible, cooled and weighed The residue is oxide of tin

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 The composition of oxide of tin is constant, and independent of the method of preparation Oxide of tin, therefore, is a compound, not a mixture or a solution

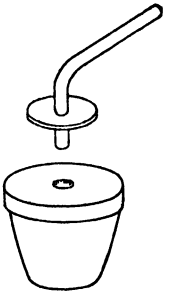


FIG 19 —Rose's crucible

The chemical elements.—The list of chemical elements, given on p. 438, comprises ninety different kinds of matter. Of these about one-half are commonly found in chemical laboratories, and of these about twenty occur in the uncombined state. About 99 per cent. of terrestrial matter is composed of some twenty elements and their compounds.

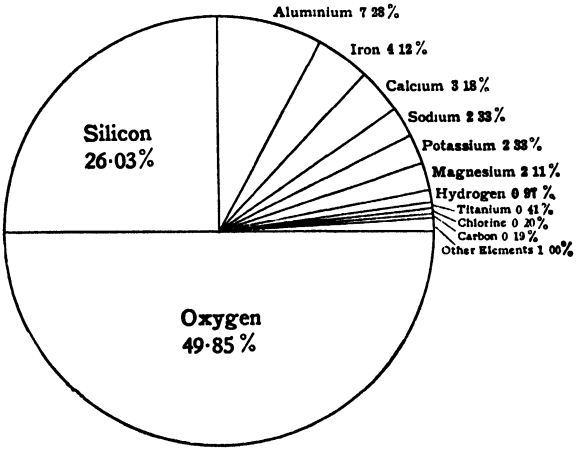


FIG. 20 —The distribution of the elements

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, and in meteorites (318 iron and 125

stone) by O. C Farrington. The following table (for the symbols see p. 438) gives the average composition by weight of these materials in parts per 100.

DISTRIBUTION OF THE ELEMENTS

Lithosphere		Hydrosphere		Atmosphere		Meteorites	
O	47 33	O	85 79	N	75 53	Fe	72 06
Si	27 74	H	10 67	O	23 02	O	10 10
Al	7 85	Cl	2·07	A	1 40	Ni	6 50
Fe	4 50	Na	1·14	H	0 02	Si	5·20
Ca	3 47	Mg	0·14	C	0 01	Mg	3 80
Na	2 46	Ca	0 05	Kr	0 01	S	0·49
K	2·46	S	0 05	Xe	0 005	Ca	0·46
Mg	2 24	K	0 04	Remainder	0 005	Co	0 44
Ti	0·46	N	0 02		—	Al	0 39
H	0 22	Br	0 01		—	Na	0 17
C	0 19	C	0 01		—	P	0 14
P	0·12	I	0 006		—	Cr	0 09
S	0 12	Fe	0·002		—	C	0 04
Mn	0 08	Remainder	0 002		—	K	0 04
Ba	0 08		—		—	Mn	0 03
F	0 07		—		—	Ti	0 01
Cl	0 06		—		—	Cu	0 01
N	0 02		—		—	Remainder	0 03
Sr	0 02		—		—		—
Remainder	0 51		—		—		—
	100 00		100 00		100 00		100 00

A combined table for the terrestrial cases is the following, due to Clarke :

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 (Fig. 20) 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 next in abundance. Nitrogen, occurring in the atmosphere, and other elements, especially carbon, 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 core must consist largely of substances of high density, probably iron with some nickel. This is surrounded by an intermediate shell of sulphides and oxides, or perhaps oxides only, of the heavier metals, and this in turn is enclosed by an outer shell of silicates.

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

By means of **spectrum analysis** (Chap XXXVII), it is possible to discover the elements present in the **sun** and **stars**. Many of the terrestrial elements occur in them, and no elements not known to us on the earth appear in the spectra.

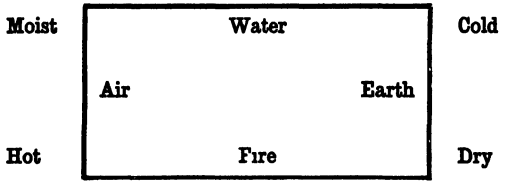
The early history of chemistry.—The conceptions underlying the definitions of elements and compounds, although now almost obvious, were reached only after centuries of effort They represent the few grains of truth remaining from the winnowing process of experimental investigation applied to the mass 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. A brief account of the development of these fundamental conceptions from the dawn of chemistry, one of the oldest of the sciences, will now be given *

The definition of an element given above dates from Robert Boyle, who, 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 **elements are the practical limits of chemical analysis,** substances incapable of decomposition by any means with which we are at present acquainted. This definition he regarded as provisional: substances regarded as elements might, with improved methods, be shown to be compounds, but until that happened they must be taken as elementary.

Theory of the four elements.—The first clear expression of the idea of an element occurs in the teachings of the Greek philosophers, beginning with Thales (640–546 B.C), who taught that all things arose from *water*. Anaximenes (560–500 B.C.) thought *air* was the primary substance, whilst Herakleitos (536–470 B.C.), impressed by the constant change of the material world, regarded the ever varying *fire* as the fundamental principle. Empedokles (490–430 B.C.) introduced the ideas of four " roots " of things: fire, air, water and earth, and two

* See the author's *Everyday Chemistry* (Macmillan), Chap. IV, for further details on the early history of chemistry.

forces, attraction and repulsion, which joined and separated them. Aristotle (384–322 B.C.) summarised the theories of earlier thinkers and developed the idea of a **primary matter**, called *hulé*, on which a specific form (*eidos*) could be impressed. The same primary matter can receive different forms, just as a sculptor can make different statues from the same block of marble, although Aristotle preferred to think of the form evolving from within, as in organic growth. The forms can be removed, and replaced by new ones, so that the idea of **transmutation of elements** arose. Aristotle's elements are really **fundamental properties** of matter, for which he chose hotness, coldness, moistness, and dryness. By combining these in pairs, as in the diagram, he obtained the **four elements**, fire, air, water, and earth:



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 his later writings as the **quintessence** or the **ether**.

The origins of chemistry.—Chemistry, or the study of the composition of substances, had its origin about the beginning of the Christian era in the Hellenistic-Egyptian city of Alexandria, and was probably the result of the blending together of material from two sources: (1) the speculative philosophy of Greece, and (2) the Egyptian practical arts of working in metals and glass, and the dyeing of tissues. The Egyptian technique, handed down in the workshops, is described in the **Papyrus of Leyden**, discovered at Thebes and preserved in the museum at Leyden. It is written in Greek and dates probably from about 300 A.D., although much of the material is probably derived from older Egyptian sources and some of the substances described are given Egyptian names (*e.g.*, *asem* for an alloy of gold and silver). The papyrus seems to have included the working notes of a fraudulent goldsmith. Recipes for *plating* base metals with gold occur in it, but the author is aware that transmutation did not occur. 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."

The earliest of the true chemical treatises, written in Greek at Alexandria during the first four centuries A.D., speak already of the *artificial*

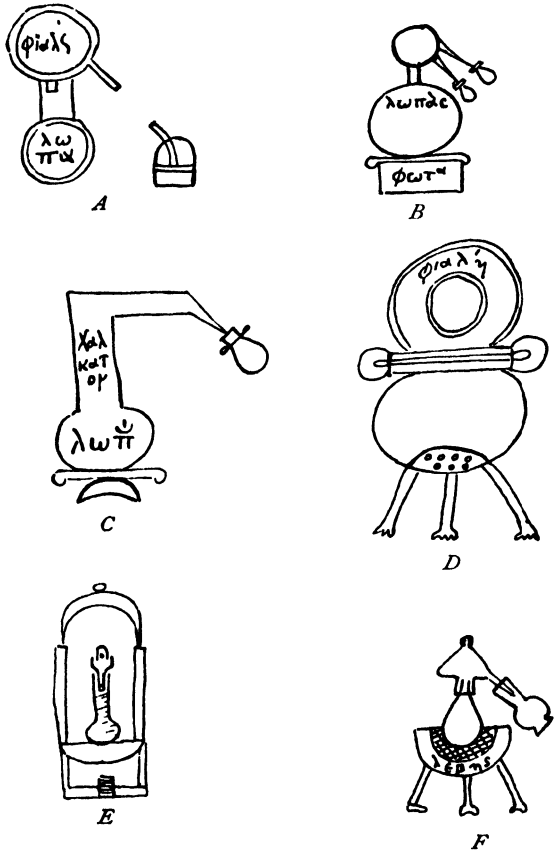


FIG. 21.—Illustrations of chemical apparatus copied from Greek MSS of Zosimos and others in the Bibliothèque Nationale, Paris The Greek names of the apparatus will not be found in the dictionaries *A*, *B*, *C* and *F* represent apparatus for distillation, *later* called alembics. In the MSS the lower part is called *lopas*, the upper *phiale* These are sometimes heated by lamps (*phota*), sometimes on a sand bath (as in *F*). *D* is a brazier, *E* an apparatus for heating a phial in a sand bath, *C* is a copper still. All this apparatus was well known before 200 A.D.

production of gold and silver and the imitation of valuable dyes. The earliest name for chemistry is the *Divine art*; the name *chemeia*

appears about 250 A D and seems to be derived from the Egyptian word *chemi*, meaning " black or burnt," or " Egyptian," or both. One of the earliest treatises is attributed to Demokritos, but is pseudepigraphic, since it is not regarded as written by Demokritos of Abdera (*c.* 500 B C), a famous natural philosopher and one of the originators of the atomic theory (p. 104), but by a Hellenistic-Egyptian author during the first century A.D. The most considerable treatise, however, is by Zosimos of Panopolis in Egypt, who lived about 250–300 A D. and first uses the name *chemeia*. These treatises, many of which are still in existence, contain descriptions of chemical apparatus, especially for distillation (Fig 21), of many chemical operations and of some substances not mentioned by earlier authors, such as Pliny (23–79 A.D.), Dioskorides (60 A.D.) and Galen (131–201 A.D.)

In 640 A.D. Egypt was conquered by the Arabs, who caused translations of Greek works on medicine and chemistry to be made by Nestorian Christians, these translations often going through the stage of Syriac before appearing in Arabic Some Syriac treatises on chemistry are known. By the end of the seventh century several Arabic translations of Greek works from Egypt had appeared, but in the eighth century there was great activity in the study and translation of Greek treatises in the new city of Bagdad, founded in 762 A D.

By this time chemistry had been in existence, in Egypt, for over five hundred years. Chemistry among the Arabs was principally cultivated by Jabir ibn Hayyan (*c* 740–813 A.D.), ar-Razi (" Rhazes ") (*d.* 925 A D.) and ibn Sina (" Avicenna ") (*b.* 980 A.D.). Jabir and Rhazes were skilled practical chemists ; Avicenna probably did not make many chemical experiments, but he wrote a book on alchemy which is quoted by Roger Bacon (1214–1292), who was very interested in the subject. Jabir was thought to be the author of a treatise known in a Latin work attributed to Geber,* but the Arabic original is not known, although some chemical works of Jabir in Arabic are in existence

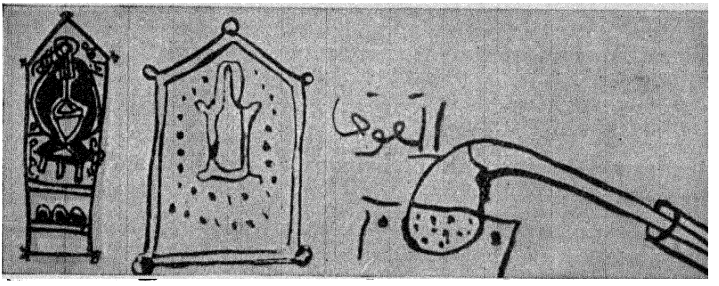
These men taught a new theory in chemistry, viz., that metals are composed of mercury and sulphur, and are generated in the interior of the earth from these materials. This theory appears in an encyclopaedia written about 950 A.D. by the members of a secret society, the Brethren of Purity, at Basra ; this work is largely compiled from Syriac translations made at a much earlier date and based on Greek sources.

A knowledge of chemistry first reached Mediaeval Europe through translations of Arabic works made principally in Spain, beginning about 1100 A.D., and important early students of the subject in Europe were Albertus Magnus in Germany (1193–1260), Roger Bacon in

* *Liber Geber*, British Museum, 1480 (?). English translation *The Works of Geber, the Most Famous Arabian Prince and Philosopher*, Richard Russell, London, 1678.

England, Raymond Lully in Spain (1235–1312 ?) and Arnold of Villanova in France (1240–1319). The great minds soon lost interest in the subject, since the supposed transmutations were found to be fraudulent.

The three alchemical elements (*tria prima*) : salt, sulphur and mercury, were said to have been introduced by Basil Valentine,



1 2. 3.

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FIG. 22.—(1) Apparatus for digestion (Syriac MS.). (2) Apparatus for digestion in small chamber (Syriac MS.). (3) Retort and receiver (Syriac MS.), a later addition. (4) An illustration from a page of a fairly modern Arabic chemical MS. in the British Museum.

supposed to have written in 1470, but probably mythical, the real author being his "editor," Thölde, 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

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

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 red powder. Some of the recipes for its preparation, in so far as they are intelligible, show that it was a salt of gold, or a solution of gold in mercury, the latter being driven off in the fire, leaving the gold

Experiments on supposed transmutation included roasting 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, iron pyrites, a yellow mineral looking somewhat like gold, was melted with lead, and the lead cupelled, when 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 contains records of frauds practised by the "adepts" on credulous dupes. 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. Most of the alchemists, however, were honest men, and in making great numbers of experiments they added much useful knowledge to practical chemistry.

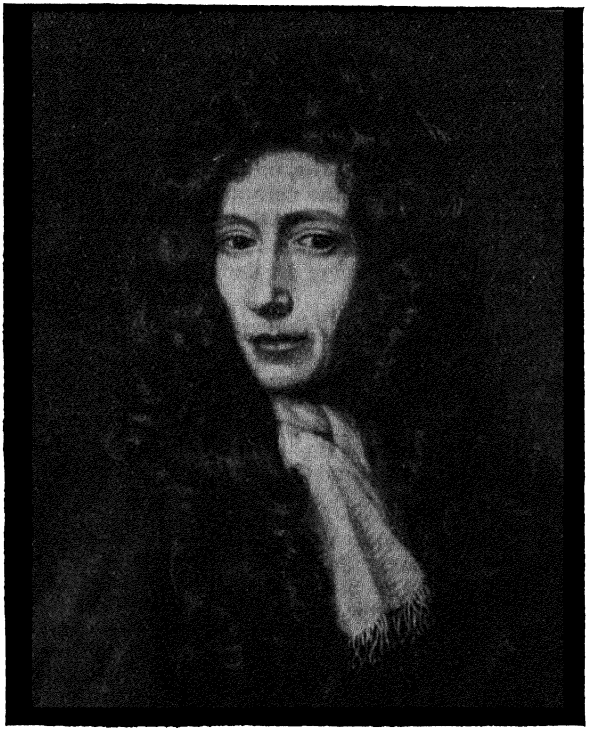
Attempts at transmutation have been made in recent times, the philosopher's stone in this case being **radium.** Ramsay and Cameron (1907) thought they had converted copper into lithium to a minute extent by exposing a solution of copper sulphate to the emanation of radium, but Mme. Curie showed that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

Iatrochemistry.—About 1525 another school of chemists arose, the **Iatrochemists,** *i e*, **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; he also believed in the philosopher's stone It was thought that the philosopher's stone and the elixir would turn out to be the same, an idea which arose partly from the Oriental imagery of the alchemists, who spoke of "healing" metals when they were transmuted, and partly because many substances, such as arsenic, mercury, and zinc, change the colours and properties of metals and also have a powerful action on the human body.

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 by an adept, and sought for the *alkahest*, or universal solvent. He considered that all materials were derived from water, as taught by Thales, and describes an experiment in which a

* *Ortus Medicinae*, Amsterdam, 1648; Engl tr, *Oriatrike or Physick Refined*, London, 1662.

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.



ROBERT BOYLE.

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 sylvestre. A gas, according to him, is something which cannot be kept in a vessel.* In

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

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 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.

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 Mass,** or the **Law of Indestructibility of Matter.**

Pure substances may be divided into **elements** and **compounds,** according as they cannot, or can, be decomposed by ordinary chemical processes. Although all elements are probably composed of two primary particles, electrons and protons, yet, in the present state of our knowledge, they are regarded as simple distinct forms of matter.

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 (*c* 1620), viz , *gas sylvestre* (carbon dioxide) and *gas pingue* (hydrogen) No new gases were discovered from then until the time of Priestley (1772) , although Stephen Hales (1727) had collected several gases over water, he did not realise their qualitative differences. The two gases of Van Helmont were carefully investigated by Henry Cavendish (1766) ; *gas sylvestre* was named **fixed air** by Joseph Black, 1754, 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, with iron and zinc, was " the same, and of the same amount, whichever acid is used to dissolve the same weight of either metal," and hence concluded that it came from the metal. Inflammable air was much lighter than common air, whilst carbon dioxide was heavier. He collected fixed air over mercury and determined its solubility in water. (" On Factitious Airs," *Phil Trans*, 1766)

Joseph Priestley (1733–1804),* 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, hydrogen chloride, ammonia, silicon fluoride, 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 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, and depend on the same cause, may conveniently be described together These are combustion, and the calcination of metals.

* *Observations on Different Kinds of Air*, 6 vols 1774–86 , abridged edition, 3 vols. 1790.

The alchemists attached great importance to the effects of heat on substances. 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 lodges around the calx. His ideas are crude.

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, did not notice, as Lavoisier did a century later, that some of the air was absorbed, although he found 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 "igneous corpuscles," 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.

EXPT 1.—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.

* *Works*, edited by Birch, 5 vols 1744; abridged by Boulton, 4 vols. 1699–1700, do. by Shaw, 3 vols. 1725.

On the basis of experiments (which were not published) 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* (1674) elaborated a theory similar to that of Hooke, and supported by descriptions of experiments. 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 2 —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 23)

(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 23), 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 refers to an experiment described by Hamerus Poppius (1625) and Le Fevre (1660), viz , calcining 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, although but a step was needed, viz. strongly heating nitre, 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 Chymie*, 1675), these

* *Tractatus quinque medico-physici*, Oxford, 1674

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

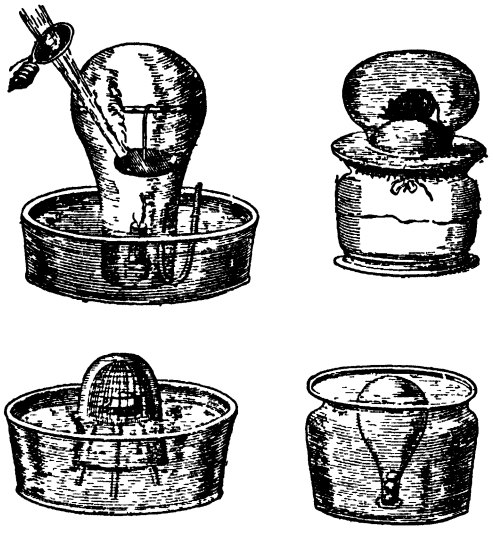


FIG. 23 —Mayow's experiments (from his *Tractatus quinque medico-physici*, 1674)

The illustrations depict the experiments on combustion and on the respiration of a mouse described in the text, also the contraction of air confined over water by the respiration of a mouse, and the collection of " air " (nitric oxide) from iron balls and dilute nitric acid in an inverted flask

Theory of phlogiston.—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.

In 1702 Becher's treatise was republished by George Ernst Stahl, professor at Halle, 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*. When bodies burn, phlogiston escapes with a rapid whirling motion; when the original bodies are recovered by reduction, phlogiston is replaced. Oil, wax, and charcoal are rich in phlogiston, and may restore it to a burnt material. Zinc on heating to redness

burns with a brilliant flame, hence phlogiston (ϕ) escapes. When the white residue of calx of zinc is heated to whiteness with charcoal (rich in phlogiston), zinc distils off: **calx of zinc** + ϕ = **zinc.** Similarly with other metals. Phosphorus burns to produce an acid matter, and much heat and light are evolved: **phosphorus** = **acid** + ϕ. 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, although Boerhaave, in his important *Elementa chemiae* (1732), does not mention it.

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.

EXPT 3.—This increase of weight is shown by experiment. Finely divided *reduced iron* is taken up by a horse-shoe magnet counterpoised

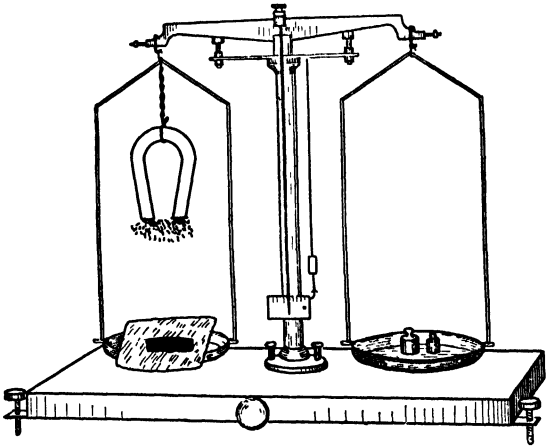


FIG 24.—Increase in weight of iron on burning.

from a balance (Fig. 24), a piece of asbestos paper being placed in the pan underneath. A spirit-lamp flame is applied to the tufts of iron, the powder begins to glow, and after calcination falls from the magnet. The pan on the side of the magnet sinks, and the iron increases in weight. The iron calx is black, whereas the original iron is grey.

Scheele's experiments on fire and air.—Carl Wilhelm Scheele (1742–1786), a poor apothecary of Sweden, made a great number of fundamental chemical discoveries, those on combustion being published in

the treatise *On Air and Fire* The 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 established in 1892, from his original laboratory notes.

In his first set of experiments Scheele measured the contraction of air standing in contact with 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 says, are rich in phlogiston or 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

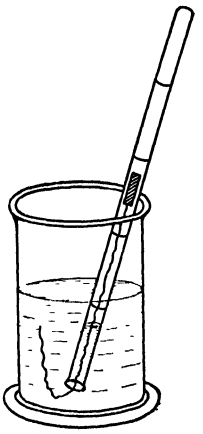


FIG 25.—Diminution of air by phosphorus

EXPT 4.—Take three glass tubes, 2 ft long and ¾ 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 a 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 cylinders of water for a few days (Fig. 25) 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 each. The flame is extinguished.

The inflammable substance was not in the residual gas, 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 [really one-fifth] of the whole mass of the air, is peculiarly disposed to such attraction." These two fluids 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. By allowing phosphorus to stand for six weeks in the same flask, until it no longer glowed, contraction of the air also occurred.

Scheele then burnt a hydrogen flame under a glass globe standing over water (Fig. 26). The water rose until it filled about one-fourth of the flask, when the flame went out.

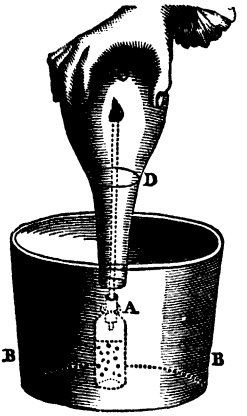


FIG. 26.—Scheele's experiment on the combustion of inflammable air.

EXPT. 5.—Burn a jet of hydrogen from a Kipp's apparatus inside a graduated bell-jar over water. The gas is turned off as soon as the flame (which becomes enlarged and very dim towards the end) goes out. After cooling, one-fifth of the air has disappeared (Fig. 27).

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, and he found nothing in the water. Scheele concluded that the fire air and phlogiston had escaped through the glass, combined in the form of heat and light, considered to be material: **fire** (or **caloric**) = **fire air** + ϕ.

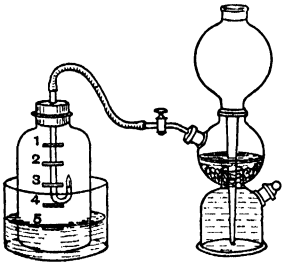


FIG. 27.—Combustion of hydrogen in air.

This hypothesis is 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 tried to reverse this change, *i.e.*, to decompose caloric into fire air and phlogiston. For this purpose he must present to the caloric a substance having a greater attraction for phlogiston than is exhibited by fire air, when the latter should be set free 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, and to set the acid free again at the high temperature, he

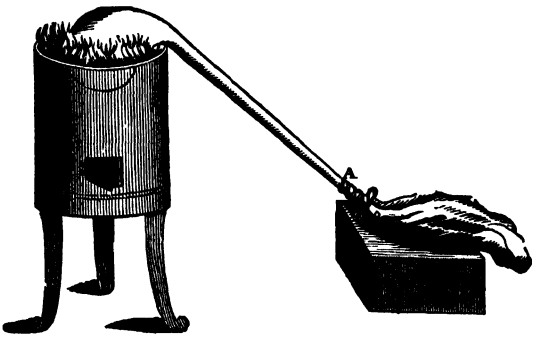


FIG 28 —Scheele's isolation of fire air

distilled the resulting nitre with strong oil of vitriol (sulphuric acid) in a retort (Fig. 28). Red fumes came off, which were absorbed in a bladder containing milk of lime, attached to the neck of the retort. The bladder gradually 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. He heated calx of mercury (*mercurius calcinatus per se*), which he supposed absorbed phlogiston from the caloric, setting free the fire air

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

He also obtained fire air by heating "black manganese" (manganese dioxide) with sulphuric or arsenic acid, nitre alone strongly, and silver or mercurous carbonates, the *aerial acid* (carbon dioxide) simultaneously produced being absorbed by means of an alkali: silver carbonate = silver + fire air + aerial acid; and finally by heating magnesium and mercurous nitrates

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 aid 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. 6.—Fill a gas-jar, divided into 5 parts, four-fifths with nitrogen, and then fill up the remaining fifth with oxygen. Test the gases separately in tubes with a taper, and then the mixture.

Scheele confined animals and insects in 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.

STATUE OF PRIESTLEY AT LEEDS.

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 filled with, and inverted over, mercury.

"Having procured a lens of twelve inches diameter, and twenty inches focal distance, 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."

Priestley modestly 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 " He was, however, a master of experiment

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). " Who can tell but that, in time, this pure air may become a fashionable article in luxury. Hitherto only two mice and myself have had the privilege of breathing it "

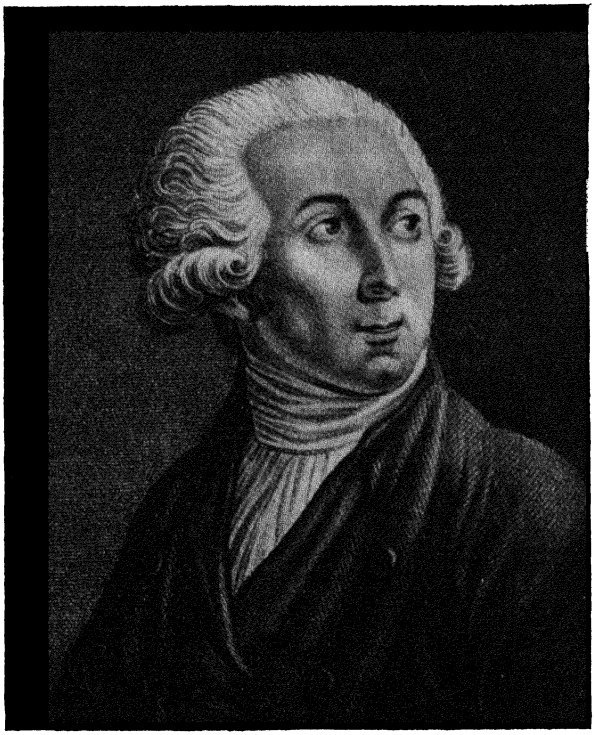
He suggested that by blowing fires with the new air, very high temperatures might be attained, and his friend Mitchill was later on able to melt platinum in this way.

Priestley 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 supports combustion because it is only partly 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, therefore the new gas must contain little or no phlogiston, and hence Priestley called it **dephlogisticated air.** The gas which is left when bodies burn out in ordinary air was named, for a similar reason, **phlogisticated air :**

Dephlogisticated Air = **Air** $- \phi$. (Scheele's **Fire Air** ; Oxygen.)
Phlogisticated Air = **Air** $+ \phi$. (Scheele's **Foul Air** ; Nitrogen.)

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 man of science, began to experiment on **combustion** in 1772. He found that metals when calcined increase in weight, as pointed out by Rey in 1630, and an equal weight of air is absorbed. In a given volume of air, calcination proceeds only to a fixed limit, and an unabsorbed gas remains. Phosphorus burns in a



LAVOISIER.

confined volume of air; the diminished volume extinguished a taper, and the white powder formed weighs more than the phosphorus. He concluded that *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 found no change in weight, which disproved Boyle's theory, until air was allowed to enter. 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."

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 Chimie* (1789), speaks of " this air, which Dr. Priestley, Mr. Scheele, and I discovered about the same time," his memory was at fault.

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

He heated 4 oz. of mercury in a retort which communicated with a measured volume of air in a bell-jar over mercury (Fig 29) The volume of air in the bell and in the retort was 50 cu in After a time red specks, and scales, of calx formed 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 (see Expt 13, Chap II) 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).

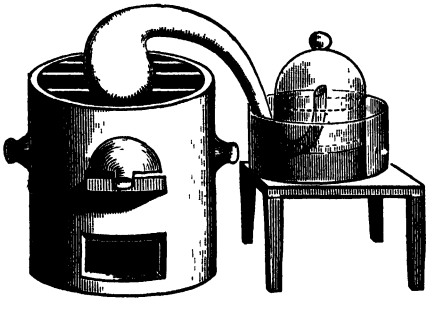


FIG. 29.—Demonstration of the composition of air by Lavoisier (1789)

Lavoisier made experiments on the combustion of substances in vital or " pure " air, and summed up his conclusions in the four statements which comprise the fundamental tenets of the **antiphlogistic theory**:

(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** (ὀξύς = *acid*).

(3) Metals produce **calces** [basic oxides] 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.

EXPT. 7.—Lavoisier's experiments may be repeated by burning sulphur, phosphorus, and carbon in jars of oxygen, the substances being held by deflagrating spoons (Fig 30), 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.

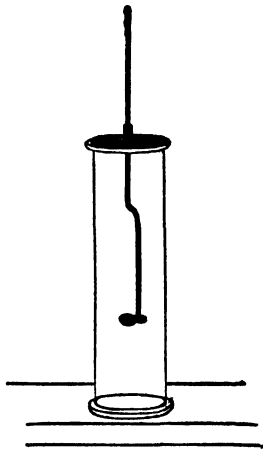


FIG 30.—Gas jar and deflagrating spoon.

Lavoisier's conclusions were not accepted at once; Black in England, and a few French chemists, supported them, but there was a difficulty still to be overcome. 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. The metal contains phlogiston as well as calx, so that in reacting with the acid it evolves this phlogiston as inflammable air. Lavoisier's theory could give no explanation of the origin of the inflammable air; this 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 Joseph Black in 1754, 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.

Further details on the subject of this chapter are given in Clara M. Taylor's *Discovery of the Nature of the Air*, Bell and Sons (Classics of Scientific Method).

CHAPTER IV

THE COMPOSITION OF WATER

The work of Cavendish.—Inflammable air was first collected by Boyle. He filled a bottle with dilute sulphuric acid, put some iron nails in it, and inverted the bottle in a dish of the acid. Bubbles of gas rose from the iron and collected in the bottle. Boyle in 1672 also described the combustibility of hydrogen and showed that a hydrogen flame is extinguished in an exhausted receiver. In 1776 Macquer noticed that a hydrogen flame deposited moisture on a cold saucer 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 1 *—Collect a mixture of 2 vols of hydrogen and 1 vol of oxygen in a strong soda-water bottle over water 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 Ignite the gas by a long taper There is a loud explosion

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

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. 2.—Burn a jet of hydrogen, dried by calcium chloride, under a glass retort, cooled by circulating cold water. Notice the collection of moisture on the outside of the retort, which drops off and may be

* This and similar experiments must be performed with adequate precautions to prevent injury in case the bottle should burst.

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.**

Cavendish 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. 31), 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*. The ratio of the combining volumes of hydrogen and oxygen found in these experiments was 201 : 100.

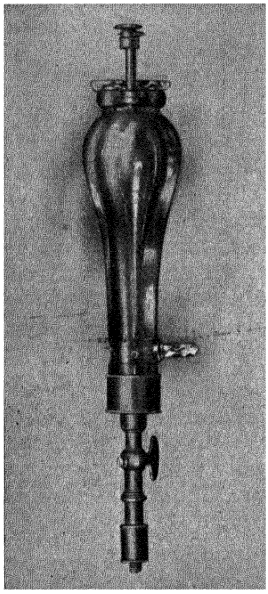


FIG. 31.—Cavendish's firing globe ("Eudiometer").

(From a photograph of what is believed to be the original apparatus in the University of Manchester.)

Cavendish proved that the acidity was due to **nitric acid,** formed only with oxygen in excess, and due to the combination with oxygen of nitrogen present in it as an impurity. Acid is not produced in the explosion of hydrogen with *air*, because the flame is not hot enough. If excess of hydrogen is used with oxygen containing nitrogen, no acid is produced, since it is reduced by the hydrogen.

Cavendish's attempts to find the cause of the acidity of the water delayed publication of his memoir until 1784. His conclusions were: "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, but in all probability the former." He represented the formation of water as follows:

$$\left.\begin{array}{l}\text{Inflammable air} = \text{water} + \phi \\ \text{Dephlogisticated air} = \text{water} - \phi\end{array}\right\} = 2 \text{ water.}$$

Cavendish took (water + ϕ) for inflammable air, because a red heat is necessary to start the combination of the two gases, whereas **nitric oxide**

(*cf.* p. 3) combines with dephlogisticated air at the ordinary temperature, and in presence of water forms nitric acid. Nitric oxide, produced by the action of copper on nitric acid, was regarded as (nitric acid + ϕ). It is improbable that dephlogisticated air should be able to separate ϕ

CAVENDISH.

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 Sir Charles Blagden, formerly Cavendish's assistant, visited Lavoisier, and told him of Cavendish's experiments. Lavoisier saw the importance of the result, and on 24th June, 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, in 1784, 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 claim to the discovery of the composition of water was dismissed by Arago, but he, nevertheless, must be given 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"

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 3.—A piece of *weldless* iron pipe, loosely packed with iron turnings, is heated to redness (Fig 32), and connected

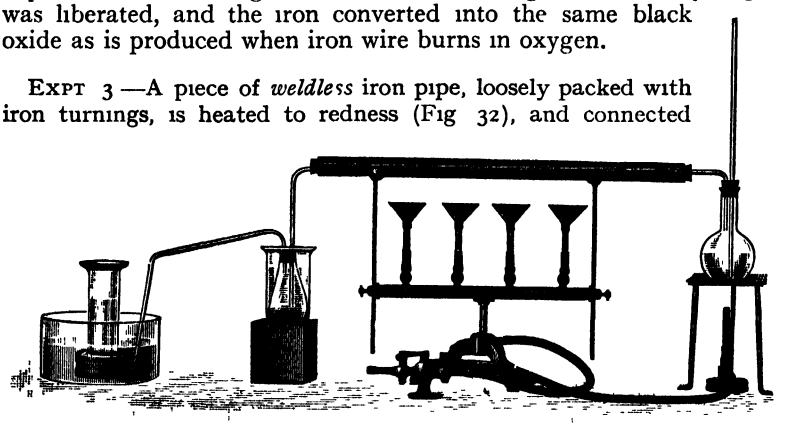


FIG 32.—Decomposition of steam by red-hot iron.

with a flask of water at one end, an empty flask and gas delivery tube being at the other, as shown. 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. Show that this is hydrogen. After the experiment, examine the residue in the tube.

EXPT. 4.—Insert a piece of burning magnesium ribbon into a large conical flask in which water is boiling vigorously. The metal burns brightly in the steam, the hydrogen produced burns when kindled at the mouth of the flask, and white magnesium oxide remains.

Monge in 1783 exploded hydrogen and oxygen, drawn from two graduated jars, in a previously evacuated glass globe with firing wires

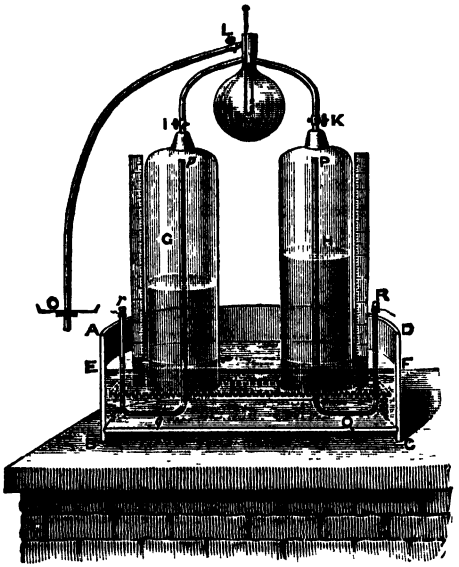


FIG 33 —Monge's experiment on the combination of hydrogen and oxygen gases.

The gases were collected through siphon-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

(Fig. 33). No fewer than 372 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.

Lavoisier was now able to explain the difficulty mentioned on p. 43, and so remove the last argument against the antiphlogistic theory. A metal, such as zinc, when dissolving in dilute acid, decomposes the water, liberating hydrogen and combining with oxygen of the water 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 the present time it is known that the hydrogen really comes from the acid.

From 1785 the theory of phlogiston gradually disappeared: it was abandoned by practically every chemist, except Priestley and Cavendish (whose work had done so much to overturn it), and modern chemistry had its origin in Lavoisier's writings. The material had been collected by the investigations of Boyle, Priestley, Cavendish, and Scheele, but it required the clear and original mind of the great French chemist to form it into a logical and harmonious system

The electrolysis of water.—In 1801 Nicholson and Carlisle, experimenting with the newly-invented electric battery of Volta, discovered that bubbles of oxygen and hydrogen, respectively, rise from two gold wires connected with the copper and zinc poles of the battery and dipped into water. From copper or iron wires hydrogen only 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 synthesis of water. Davy in 1806 showed that when 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. *Water is decomposed by the electric current into hydrogen and oxygen in the ratio of 2 to 1 by volume.*

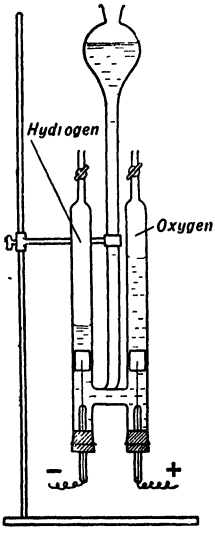


FIG. 34.—Decomposition of water into hydrogen and oxygen by electrolysis.

EXPT 5.—An apparatus for the decomposition or **electrolysis** of water by the current is shown in Fig. 34. It is called a **voltameter** or **coulometer**, and consists of two glass tubes with stopcocks above, connected by a horizontal tube, carrying a funnel for filling the apparatus with water to which a little sulphuric acid has been added to render it a conductor of electricity. Pure water is a bad conductor, but only the water is decomposed in the process The **electrodes** leading the current into and out of the liquid consist of platinum foil. The current may conveniently be taken from accumulators in series.

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 (according to Faraday because the platinum is

cleaner), occupies 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 flame, and is **hydrogen.**

EXPT 6 —**Electrolytic gas.**—Two electrodes are placed in a bottle of dilute acid (Fig 35) the hydrogen and oxygen gases come off mixed together in the form of **electrolytic** or **detonating gas.** This is washed from acid spray by a little water in the bulb tube, and collected over

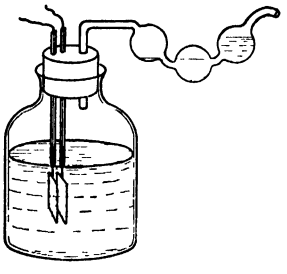


FIG 35 —Preparation of electrolytic gas

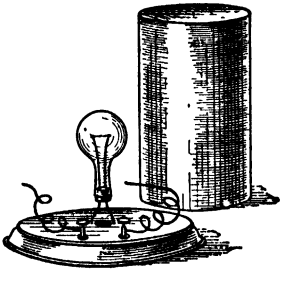


FIG 36 —Explosion of electrolytic gas by an electric spark.

water in a small *thin* glass flask. This, when filled with the mixture, is inverted over a cork carrying two copper wires connected with a coil (Fig 36) 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 fine powder escaping through the gauze in the form of smoke.

The composition of water by volume.—The composition of water by volume may be ascertained fairly accurately by the following experiment (see p. 177 for a very accurate method).

EXPT 7 —A glass **Bunsen's eudiometer,** graduated in mm and having two platinum wires at the closed end for passing a spark, is filled with, and inverted, over mercury (Fig 37).

Pure dry oxygen is introduced into the tube and the volume read off accurately, this being reduced to 0° and 760 mm. (p 59). An *excess* of pure hydrogen (about 5 vols to 1 vol. oxygen) is next added, this being found from the total volume of mixed gas, also reduced to 0° and 760 mm The total volume of mixed gas should not occupy more than one-third of the tube. The eudiometer is then pressed down on a rubber-pad and a spark passed

The volume of residual hydrogen, after cooling, is read off and reduced to 0° and 760 mm , a drop of water being added to saturate the moist gas with water and a correction for this being applied (p. 66).

In this way Bunsen, in several experiments, found that almost exactly 2 vols. hydrogen and 1 vol. oxygen combined to form water. More exact experiments show that the ratio is probably very nearly 200·29 . 100 at S.T P. (Chapter XII).

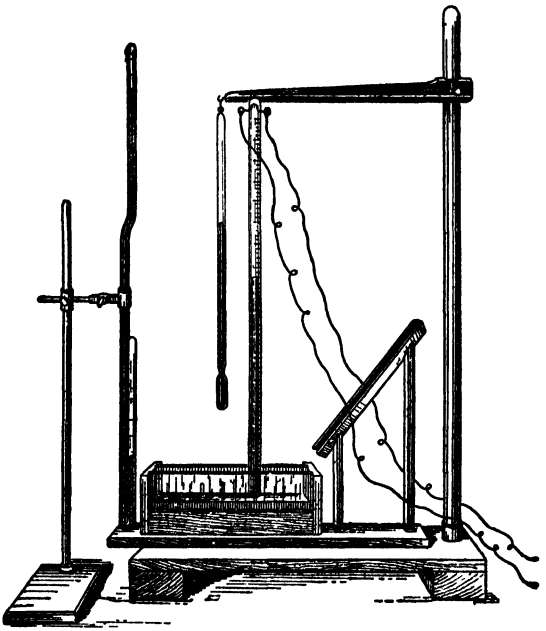


FIG. 37.—Bunsen's eudiometer for explosion of gases by an electric spark

EXPT 8.—By using a U-shaped eudiometer, the graduated limb of which is surrounded by a glass jacket through which the vapour of amyl alcohol (131°–132°) is passed, the water produced by the explosion is kept in the form of vapour (Fig. 38). The amyl alcohol is boiled in a flask and the vapour introduced through a tube at the top of the glass jacket. The vapour passing out of the jacket by the lower tube is led to a condenser Thirty c.c. of electrolytic gas are introduced into the eudiometer through a narrow tube passing down the open limb and slightly curved at the end. This volume is measured at the temperature of the jacket, with the mercury levels adjusted to equality on both sides. The open end of the U-tube is firmly closed by the thumb, and a spark passed. There is a flash and an immediate contraction. 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

The composition of water by weight.—Since it is difficult to weigh with accuracy large volumes of hydrogen and oxygen the composition of water by direct synthesis from its elements has been attempted only comparatively recently. Formerly an indirect method was used A stream of dry hydrogen, which is not weighed, is passed through a weighed tube containing 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 in a weighed calcium chloride tube 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.

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.

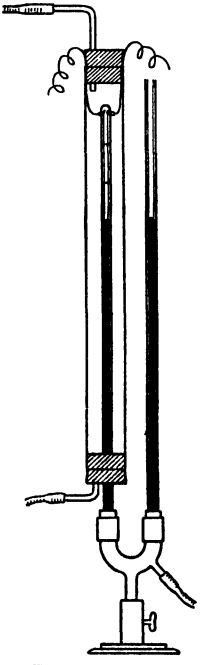


FIG 38.—Volumetric composition of steam.

EXPT. 9 —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, is introduced into a hard glass (Fig. 39), which is then weighed. The tube is connected by a rubber stopper to a weighed U-tube, filled with granular calcium chloride, which readily absorbs water vapour.

A current of hydrogen, generated from pure zinc and dilute sulphuric acid in the flask, and dried by a calcium chloride tube, is passed through the apparatus until all the air is expelled The copper oxide is then heated. Drops of moisture condense in the tube, and the black oxide of copper is reduced to red metallic copper As the experiment proceeds and the tube becomes warm, all the water is driven over into the calcium chloride tube. The apparatus is allowed to cool, with hydrogen still passing. The copper tube and the U-tube are again weighed.

In 1842 Dumas carried out this experiment with greater accuracy. Hydrogen, generated from zinc and dilute sulphuric acid, was purified

by passing through a train of seven U-tubes containing: (1) lead nitrate solution to remove sulphuretted hydrogen, (2) silver sulphate solution to remove arseniuretted hydrogen, (3) three tubes of caustic potash to remove acid vapours, (4) two tubes of sulphuric acid cooled

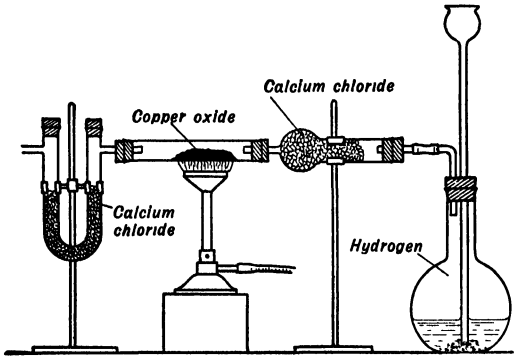


FIG 39 —Composition of water by weight

in ice, or else phosphorus pentoxide, to dry the gas The reagents were distributed on pumice or broken glass to expose a large surface. These are followed by a *témoin* (or " witness ") tube, the weight of which must remain unchanged when the drying has been as effective as possible: it contained sulphuric acid or phosphorus pentoxide.

The copper oxide was contained in a large hard-glass bulb with a long neck, weighed after evacuation to remove 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. 40.

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

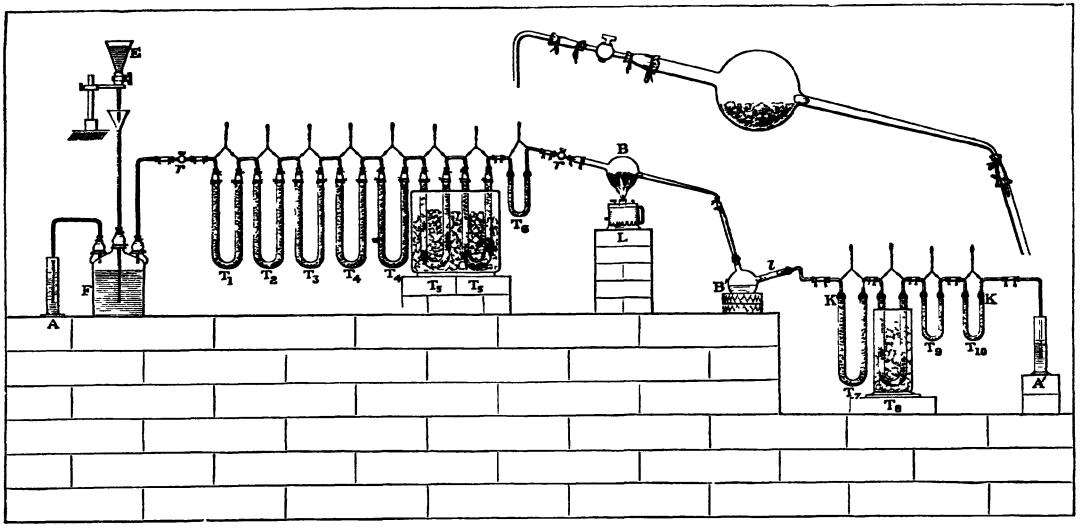


FIG 40.—DUMAS' APPARATUS FOR DETERMINING THE COMPOSITION OF WATER.

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 solution spread on broken glass; T_2, a tube containing glass moistened with silver sulphate solution; 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* tube containing phosphorus pentoxide (or sulphuric acid 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, or sulphuric acid; T_{10}, a guard-tube of phosphorus pentoxide (not weighed) to exclude moisture; A', escape-valve for excess of hydrogen, containing sulphuric acid.

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, 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

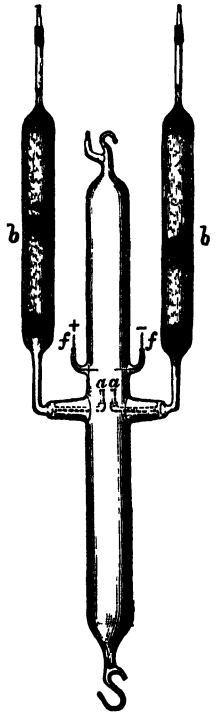


FIG. 41.—Morley's combustion tube

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

Both errors tended to reduce the loss of weight of the bulb, so that the proportion of oxygen found should be too small. All later experimenters found, however, that the proportion of oxygen given by Dumas was rather too large.

Keiser in 1888 introduced the method of weighing the hydrogen absorbed in metallic palladium (p. 61); he weighed the water formed on pumping the gas over heated copper oxide, which was not weighed. Oxygen was found by difference.

Noyes in 1890 burnt hydrogen in a copper oxide bulb and condenser made in one piece, the increase in weight 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.

Very exact experiments on the composition of water by weight were made by the American chemist, 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. 41), 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. 61, 178), Morley found the ratio:

Oxygen : hydrogen = 7·9395 : 1.

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 **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. By method (2) Morley (1895) found 1 . 7·9396.

Further details of the subjects of this chapter are given in the author's *Composition of Water*, 1928, Bell and Sons (Classics of Scientific Method).

CHAPTER V

THE PHYSICAL PROPERTIES OF GASES AND VAPOURS

Effect of pressure on the volume of a gas.—Boyle's Law (1662) states that: *when the temperature is maintained constant the volume of a given mass of gas is inversely proportional to the pressure*.

$$\therefore pv = \text{constant} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The **density** of a gas is the mass per unit volume, m/v, hence *the density is proportional to the pressure.*

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*

At very low pressures (0·01–1·5 mm. Hg) no deviation from Boyle's law can be detected (Rayleigh, 1901–2), and the gases behave as ideal (see p. 121).

Effect of temperature on the volume of a gas.—Dalton in 1801 observed that gases expanded by equal increments of volume 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

* Liquid at pressures greater than 90 atm.

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 usually known as **Charles's law**: *at constant pressure all gases expand by 1/273 of their volume at 0° C. for a rise in temperature of 1° C.*

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°, then:

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

The value $(t_1 + 273)$ is 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 $t_2 = -273$° C., then $T_2 = 0$, and by substitution in the equation we find that $v_2 = 0$. The temperature -273° C. is the zero of absolute temperature, or the **absolute zero.** By the rapid evaporation of liquid helium in a vacuum, Kamerlingh Onnes obtained a temperature of 0·82° above 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, the equation · $p_1v_1/T_1 = p_2v_2/T_2$: or, generally, $pv/T = constant$, for a given mass of gas, can be deduced from Boyle's and Charles's laws as follows ·

Change from the initial state (p_1, v_1, T_1) to the final state (p_2, v_2, T_2) in two steps :

(i) p_1 to p_2 keeping T_1 constant. Let v_1 become V. By Boyle's law: $V = p_1v_1/p_2$.

(ii) T_1 to T_2 keeping p_2 constant. V changes to v_2. By Charles's law: $v_2/T_2 = V_1/T_1$. Eliminate V:

$$\therefore\ p_1v_1/T_1 = p_2v_2/T_2.$$

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 For the ideal gas the coefficient of expansion is 1/273 09 = 0·0036618.

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, is the weight in grams of 1 litre (or 1000·028 cm.^{3}) of the substance, measured at a

temperature of 0° C., and under a pressure of 760 mm. of mercury at 0° C, the weights being reduced to sea-level, and latitude 45°.

One **litre** is the volume occupied by 1 kilogram of water, at 4°, weighted in vacuum at sea-level, and latitude 45° One **cubic centimetre**, 1 cm ^{3}, is the capacity of a centimetre cube, the centimetre being one-hundredth of the length of the standard metre Owing to inconsistency in the Metric System the volume of 1 gram of water at 4° is not 1 cm ^{3}, but 1·000028 cm.^{3} The volume of 1/1000 of the standard litre (usually called "1 c c") is now called a **millilitre**, ml In this book c c is used when no particular accuracy is involved, since it is a very familiar expression

(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° C. at sea-level, and at latitude 45°. On account of slight deviations of gases from Boyle's and Charles's laws the density in accurate work is determined with the gas actually at S.T.P., so that no corrections by the gas laws are necessary. With vapours an approximate value of the relative density is all that is 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 (see p. 72).

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. 17), which will vary with the moistness of the air. To eliminate these difficulties so far as possible, Regnault in 1845 made use of **compensating globes.** The density globe was counterpoised on the balance by hanging on the other arm a second globe of as nearly as possible identical weight and volume (Fig. 42), 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 required in this method was pointed out by Rayleigh (1882), 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 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

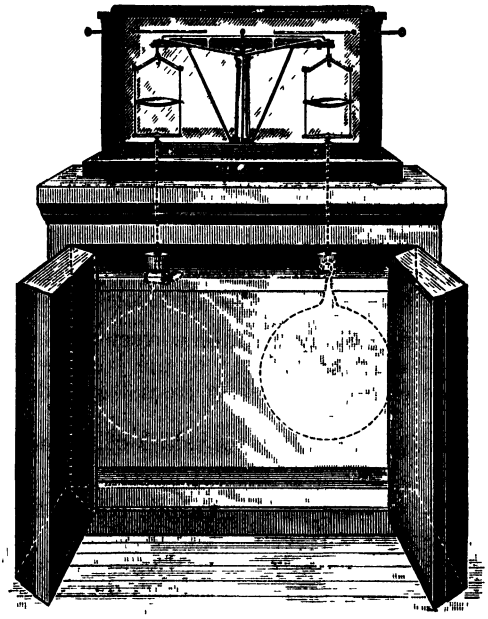


FIG 42 —Determination of the density of a gas

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 was raised to 0·08988.

This method was used by Morley (1896) in a determination of the normal densities of hydrogen and oxygen. Very pure hydrogen gas was absorbed in metallic palladium contained in a glass tube. This metal takes up about 600 times its own volume of hydrogen, but not of gaseous impurities, so that the latter are removed by pumping out the tube. On heating the palladium to dull redness, pure hydrogen is evolved, and the loss in weight of the tube gives the weight of gas. The hydrogen was received in three large exhausted 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

$$= \frac{3\ 7164}{43\ 3489} \times \frac{760}{725{\cdot}4} \times 1\ 00044 = 0{\cdot}089861 \text{ gm /litre}$$

As a mean result, 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 exact values of the **normal densities** of some gases :

Air	1·2927	Carbon monoxide	1·2504
Oxygen	1 42900	Carbon dioxide	1 9768
Hydrogen	0 08987	Hydrogen chloride	1 6392
Nitrogen	1·2507	Sulphur dioxide	2 9267
Argon	1·7836	Helium	0·1785
Nitrous oxide	1·9777	Neon	0 8999
Nitric oxide	1 3402	Methane	0 7168
Ammonia	0 7708		

The relative density of air is 1·2927 ÷ 0·08987 = 14·38. Densities of gases were previously referred to air = 1 instead of to hydrogen = 1 ; these values may be converted to modern units by multiplication by 14·38. The composition, and therefore density, of air vary slightly in different localities, hence this gas is no longer used as a standard of relative density.

The law of partial pressures.—When 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.)

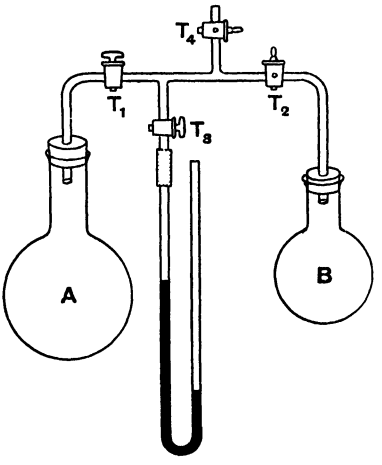


FIG 43.—Experiment on the law of partial pressures

EXPT. 1.—Connect two globes, A and B (Fig. 43), of capacities about 2 and $\frac{1}{2}$ litres, respectively, with each other and a manometer as shown. A contains air and B carbon dioxide. Close the stopcocks T_2 and T_3 and partly 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 air. Let the pressure in A be p_A mm., and the pressure in B, p_B mm. Close T_3 and open T_1 and T_2. When the two gases have mixed open T_3 and read the final pressure, p. Total volume $= v_A + v_B$, $\therefore$ partial pressures of the gases 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 gas 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.

In an 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 $= 44 + 16\ 2 = 60.2$ cm.

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.

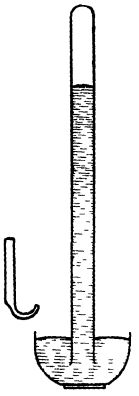


FIG 44.—Vapour pressure of a liquid in a vacuous space

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 also shows that the vapour pressure of a liquid in a closed vessel filled with an indifferent gas will be the same as if the space were initially vacuous. If insufficient liquid be present to saturate the space, the vapour is unsaturated.

EXPT 2.—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. 44) introduce a few drops of water into one tube, and a few drops of ether into the other Notice that the depression of the mercury due to the ether is much greater than that caused by the water Measure the levels and find the **vapour pressures** at atmospheric temperature. Warm the tube containing ether with the hand and notice the further fall of mercury, due to the increase of vapour pressure with temperature

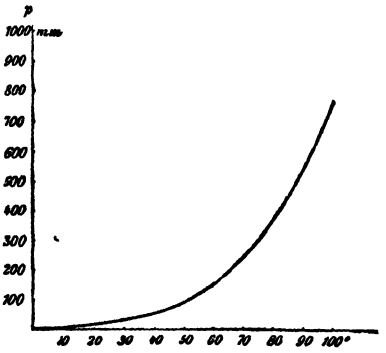


FIG 45.—Vapour pressure curve of water

The vapour pressure of a liquid rises very rapidly with the temperature. This is evident from Fig. 45, 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** is the temperature at which the vapour pressure of a liquid

becomes equal to the atmospheric pressure, or other total pressure, acting on the surface. Boiling points are usually given for a pressure of 760 mm., or 1 standard atmosphere.

If the pressure on the surface is reduced, say by connecting a flask containing the liquid with a pump, the boiling point is lowered. At a pressure of 17·4 mm., water boils at 20°. It is necessary to specify the pressure in giving a boiling point, unless this is done 760 mm. is understood 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. 2).

EXPT 3.—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

EXPT 4.—Place a thin glass bulb, containing 2 c c of bromine (Fig 46) inside a 500 c c bottle Fit to the bottle a rubber stopper, 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

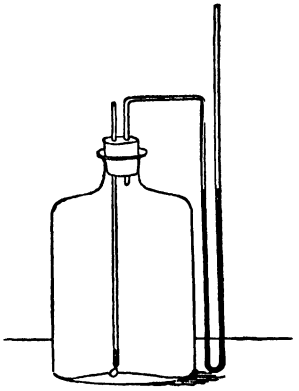


FIG 46.—Vapour pressure of a liquid in a space filled with gas

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

EXPT. 5.—Pass a small piece of camphor into the vacuous space in the barometer tube (Expt 2) surrounded above by a hot-water jacket, and notice the fall of the mercury.

Equilibrium.—At a given temperature, liquid (or solid) and vapour can exist indefinitely in contact when the vapour pressure is the

maximum at that temperature, *i e.*, when the vapour is saturated. The system composed of two phases, liquid and vapour, is then in **equilibrium.** An equilibrium state is one which is independent of time. If we represent transition from liquid to vapour by the symbol: [Liquid] → [Vapour], *i e*, **evaporation,** and transition from vapour to liquid by: [Vapour] → [Liquid], *i e*, **condensation,** the state of equilibrium will be represented by [Liquid] ⇌ [Vapour].

The equilibrium state between two phases of a pure substance is characterised by a definite pressure, which is independent of the amounts of the two phases present and depends only on the temperature (see p 87).

Moist gases.—In the laboratory, gases are often collected over water, and in accurate measurements of the volume of the gas it is necessary to correct for the water vapour contained in it. When water evaporates into a dry gas at constant pressure, the gas will expand. The volume of a given mass of gas is therefore greater, and its density is smaller, 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, $100 \times \frac{747\,3}{760}$ c c., and at 0° this would be $100 \times \frac{747\,3}{760} \times \frac{273}{288} = 93{\cdot}2$ 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 applies only, 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.

$t°$ C.	p mm	$t°$ C.	p mm	$t°$ C.	p mm	$t°$ C.	p mm
0	4·579	18	15 477	28	28 349	92	566 99
5	6 543	19	16 477	29	30 043	93	588 60
10	9 209	20	17 535	30	31 824	94	610 90
11	9 844	21	18 650	40	55·324	95	633 90
12	10 518	22	19 827	50	92 51	96	657·62
13	11·231	23	21 068	60	149 38	97	682 07
14	11 987	24	22 377	70	233 7	98	707·27
15	12 788	25	23 756	80	355 1	99	733 24
16	13 634	26	25 209	90	525 76	100	760 00
17	14 530	27	26 739	91	546 05	110	1074 6

Intermediate values in the practically useful ranges 0°–30° and 90°–100° may be obtained by interpolation

EXAMPLE.—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 ; $f=15\,48$ mm (from table) ; $t=18°$

$$\therefore \text{ required volume} = 175 \times \frac{749-15\,48}{760} \times \frac{273}{273+18} = 158{\cdot}5 \text{ c c}$$

Humidity.—The weight of aqueous vapour 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.

When a known volume of air at a known temperature and pressure is drawn by means of an aspirator through a weighed series of U-tubes containing calcium chloride, or pumice soaked in sulphuric acid, the moisture is absorbed and the weight of moisture in a given volume of air is found. 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) would be 0·8038 gm. If the hygrometric experiment shows that x gm. of aqueous vapour were contained in 1 litre of the air, this, divided by the amount contained when the air is *saturated*, found from the table below, gives 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 $t°$,

$$w = 0{\cdot}8038 \times \left(\frac{f'}{760} \times \frac{273}{273+t}\right),$$

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, calculated by the equation above 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.

$t°$ C.	w gm.	$t°$ C	w gm.	$t°$ C	w gm.	$t°$ C.	w gm.
0	0·00484	8	0 00827	16	0 01362	24	0 02173
1	0 00519	9	0 00881	17	0 01447	25	0 02302
2	0 00556	10	0·00940	18	0 01536	26	0 02437
3	0·00595	11	0 01008	19	0·01629	27	0 02574
4	0 00636	12	0 01066	20	0·01729	28	0 02720
5	0 00680	13	0 01134	21	0 01838	29	0 02872
6	0·00726	14	0 01206	22	0 01941	30	0 03032
7	0·00775	15	0 01282	23	0 0205.		

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 is justified This is very nearly the case at the ordinary atmospheric temperature

Density of a moist gas.—Consider 1 litre of moist gas at $t°$, under a pressure P mm., and let f' be the partial pressure of aqueous vapour in the gas. f' = *saturation pressure at* $t°$ (from table of vapour pressures) × *humidity*. The volume of the *dry* gas at S.T.P. will be .

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

Let the weight of 1 litre of dry gas at S.T.P. $= D$ gm. The weight of the dry gas will be :

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

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 0·8038 gm., the weight of the aqueous vapour in 1 litre of moist gas will be :

$$0{\cdot}8038 \times \frac{f'}{760} \times \frac{273}{273+t} \text{ gm.}$$

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

$$D \times \frac{P-f'}{760} \times \frac{273}{273+t} + 0{\cdot}8038 \times \frac{f'}{760} \times \frac{273}{273+t} \text{ gm.}$$

$$= \frac{273}{(273+t)\,760}\{D(P-f') + 0{\cdot}8038f'\} \text{ gm.}$$

The calculation applies to air, the appropriate density being 1·2927. The equation will also give the density of the dry gas at S.T.P. (viz., D) from the density of the moist gas.

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 ; vapour pressure of water at 15° = 12·79 mm , hence required weight

$$= \frac{273}{(273+15)\,760}\{0\cdot08987(740-12\cdot79)+0\cdot8038\times12\cdot79\} = 0\cdot09431 \text{ gm}$$

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

A similar type of calculation will give the density of any mixture of gases when the partial pressures, and the normal densities at S T P , are known.

Vapour densities.—Since vapours far from their points of liquefaction obey approximately the same laws of expansion as gases, the **vapour density**, Δ, may 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. (or ml) of hydrogen at a temperature $t°$ and under a pressure of P mm. is :

$$V \times 0\cdot00009 \times \frac{273}{273+t} \times \frac{P}{760} \text{ gm.}$$

The vapour density of a volatile liquid or solid may be determined by one or other of the three 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

Hofmann's method.—In this method (A. W. Hofmann, 1868), a barometer tube is surrounded with a glass jacket through which the vapour of a liquid boiling in a separate vessel is passed. Uniformity of temperature is thus assured. The liquid is weighed into a small bulb (Fig. 47) 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 and the liquid volatilises. The barometer is a wide tube, at least 1 metre in length, carefully graduated (Fig. 48). The bulb must be completely filled with 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. 47.—Bulb for liquid

In Hofmann's method the volume of a given weight of vapour is determined.

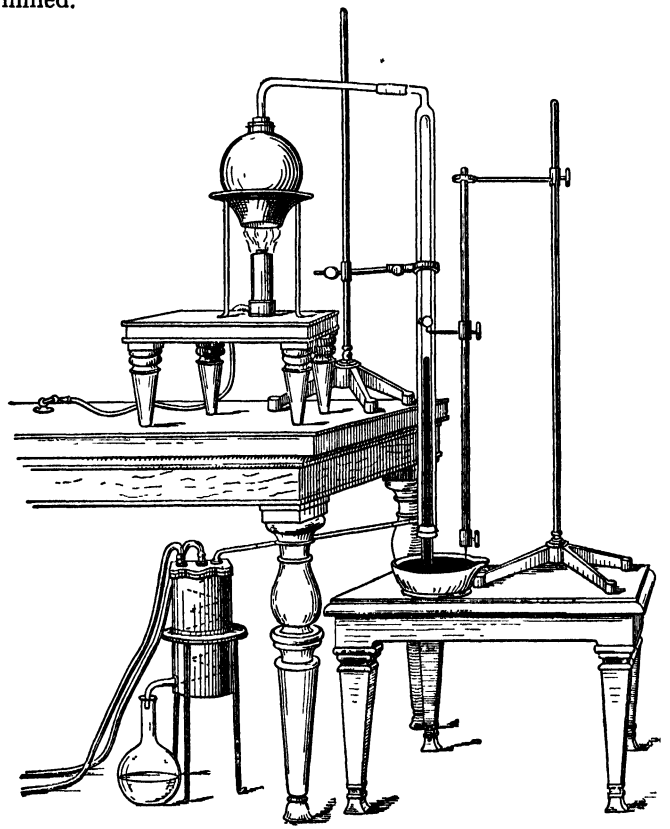


FIG 48 —Hofmann's method for determination of the vapour density of a liquid

The following liquids may be used for the vapour-jacket the boiling points at 760 mm pressure are stated

Water, 100°.	Toluidine, 202°.
Amyl alcohol, 131°–132°.	Ethyl benzoate, 212 9°
Aniline, 184·4°.	Amyl benzoate, 262°.

Since volatilisation occurs more readily under diminished pressure, steam may often be used in the jacket for 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, or a thermometer hung in the 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.

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

$\therefore$ 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. 60) and the weight of a given volume of vapour is determined. 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.

In Dumas' method a thin glass bulb (Fig. 49) 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 quickly immersed 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. 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.

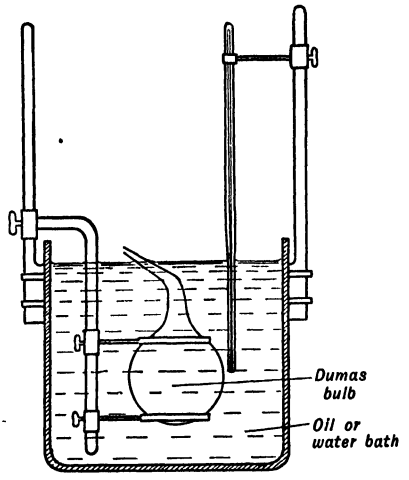


FIG 49 —Dumas' vapour density apparatus

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 the weight of vapour filling the globe $= m_1 - (m - A)$ gm.*

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

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

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

* Strictly speaking, the density of atmospheric air containing some carbon dioxide and moisture should be used According to Kohlrausch it is usually sufficient to take, as an average, the density at S.T.P. as 0·001295.

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

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

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

$\therefore$ weight of vacuous globe = 23 449 − 0 218 = 23 231 gm ;
$\therefore$,, ,, vapour = 23 720 − 23·231 = 0 489 gm

Weight of hydrogen filling globe at 110° and 759 mm

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

$\therefore$ vapour density $\Delta = 0 \cdot 489 / 0 \cdot 0114 = 42 \cdot 9$

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 (606°), cadmium (767°), or zinc (918°), in an iron bath, 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.

Victor Meyer's method.—In Victor Meyer's **displacement method** (1878), the volume of *air* displaced by a known weight of vapour is determined. It 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. 50), 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 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 *g*, filled with water, 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 dry 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*.

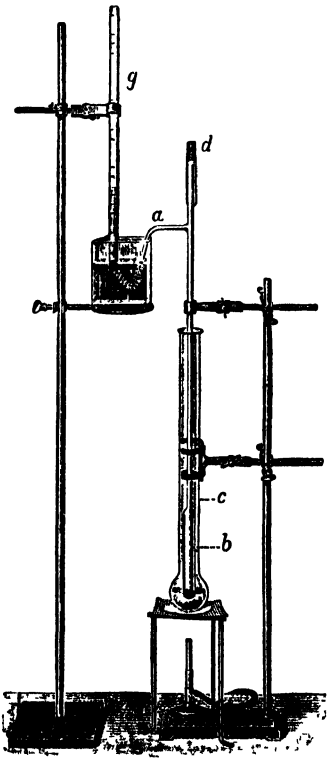


FIG 50.—Victor Meyer's vapour density apparatus

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 tube *g* is closed with the thumb, transferred to a tall cylinder of water and the water levels are equalised. 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. 67), 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 0·00009 V_0 gm , so that if m gm. of substance were used, we have :

$$\text{vapour density } \Delta = m/0{\cdot}00009\, V_0.$$

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.

$$\therefore \text{ volume of dry air at S.T P.} = 20 \times \frac{273}{288} \times \frac{770-13}{760} = 18{\cdot}9 \text{ c.c.}$$

Weight of an equal volume of hydrogen = 18·9 × 0·00009 gm. = 0·0017 gm.

$\therefore$ vapour density of chloroform = 0·1008/0·0017 = 59·3.

* The equation holds if the tube *b* was originally filled with *dry* air If the partial pressure of water vapour in the air filling the tube at the beginning of the experiment was h, the factor $(H-f)$ becomes $(H-f+h)$. The difference in the result does not usually exceed the experimental error.

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 125), 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

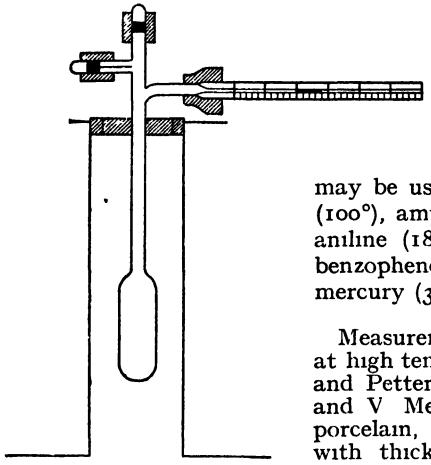


FIG 51 —Nernst's apparatus for vapour densities at high temperatures

The following substances may be used in the heating bath water (100°), amyl alcohol (132°), xylene (140°), aniline (184 4°), ethyl benzoate (212 9°), benzophenone (306°), diphenylamine (310°), mercury (357°), sulphur (444·6°)

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 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 51)

A more sensitive micro-balance, reading to 1/500,000 mgm , was used by Ramsay and Gray (1911) in determining the density of radium emanation, o 1 cu. mm , less than o 001 mgm , being used It consists (Fig. 52) of a beam, *A*, of quartz rods, 10 cm long, weighing o 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

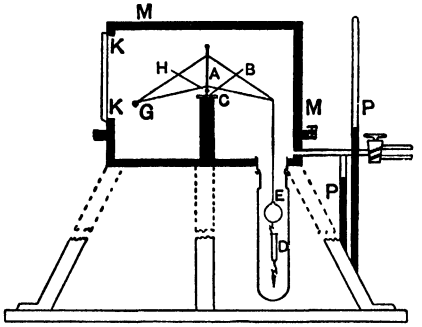


FIG 52 —Micro-balance

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

SUMMARY OF CHAPTER V

Physical properties of gases :—Boyle's law (1662) *when the temperature is constant the volume of a given mass of gas varies inversely as the pressure*: **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 $T = t° + 273$, 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 . $pv/T = \text{const}$

3 The **normal density** of a gas is *the weight in grams of* 1 *litre* (1000·028 cm^3) *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 ml [" 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).

CHAPTER VI

SOLUTIONS AND THE PHASE RULE

Solutions.—Solid sugar, or salt, when added to water, dissolves and forms a homogeneous solution. Liquid alcohol and water also mix in all proportions to form solutions It is generally possible, by suitable means, to separate again the constituents of solutions, one method being by distillation. In this, the solution is heated and the vapour of

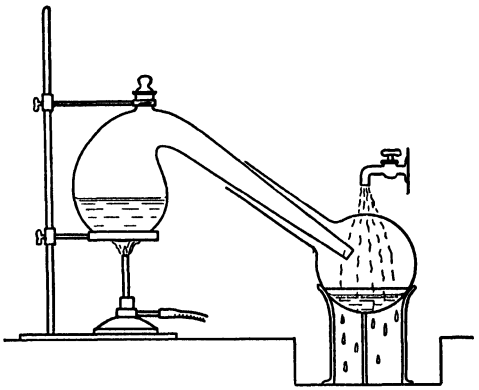


FIG. 53.—Retort and receiver arranged for distillation

the volatile liquid is condensed again by cooling Non-volatile substances (salt or sugar) remain in the residual solution, or form a solid residue. This method of separation makes use of the differences in vapour pressure of the components of a solution, at the same temperature.

A simple apparatus for distillation consists of a retort with the neck passing into a glass flask, or receiver, which is cooled by a stream of cold water (Fig. 53). If tap water is distilled in this apparatus, the dissolved mineral matter remains in the retort, and distilled water collects in the receiver. If the water contains volatile impurities, these pass over with the distillate. When larger quantities of a liquid are to be distilled it is more convenient to use a **Liebig's condenser**

(Fig. 54), 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

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.** When a mixture of equal volumes of alcohol (b pt. 78·3°) and water (b pt 100°) is distilled, the boiling point at the commencement of the operation is 84°. The liquid collecting in the receiver is

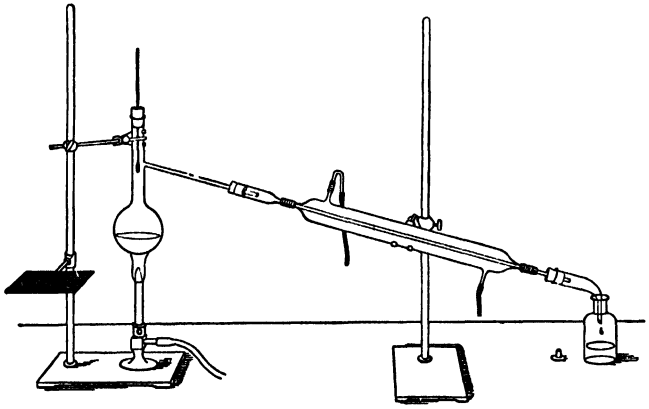


FIG 54 —Distilling apparatus with Liebig's condenser.

richer in alcohol than the original mixture, and will burn when lighted in a dish As distillation proceeds, the boiling point rises, and the distillate becomes richer in water. If distillation is stopped when one-fourth of the mixture has passed 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.**

True solutions are *homogeneous* (p. 4), and the dissolved substance is in an extremely fine state of subdivision. One gm. of eosin gives a distinct fluorescence (p. 6) 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. of dye.

Colloidal solutions, such as that of arsenic trisulphide (p 9), pass through filter papers, and do not settle out on standing, ; their heterogeneous character, however, is disclosed by the ultra-microscope. Colloidal solutions 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. 6).

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**. 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.

Solutions of gases in liquids.—If a flask and delivery tube are completely filled with tap water, and the flask heated, bubbles of gas appear, which pass out of the delivery tube under water, and will be found to be mainly air; such water, therefore, contains dissolved gas

Solids are also capable of dissolving gases, thus palladium dissolves hydrogen (p. 61), forming a **solid solution**. Solids may also dissolve solids: 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.

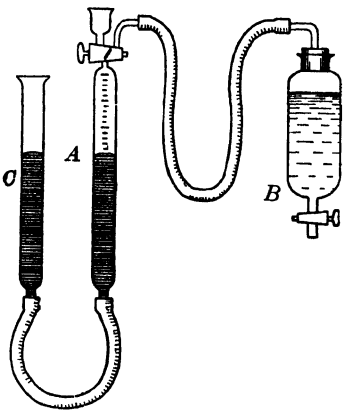


FIG. 55.—Absorptiometer

Solutions of gases in liquids may be studied by the apparatus shown in Fig. 55, called an **absorptiometer**. The gas is measured over mercury in the burette, *A*, and the volume reduced to S.T.P. Part of the gas is then passed into the absorption vessel, *B*, the volume of liquid, *e g*, water, remaining in contact with the gas being the original volume minus the volume run out. The gas 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 corrected for the vapour pressure of the liquid, temperature and

barometric pressure. The volume of gas, reduced to S.T.P., which saturates 1 volume 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 is 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 fixed volume of a liquid at a constant temperature is proportional to the pressure.*

Since the volume of a given amount of gas is inversely proportional to the pressure, *a given volume of liquid absorbs the same volume of gas at all pressures.*

Solubility of a mixture of gases in a liquid.—*The amount of any one gas dissolved from a mixture of gases 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 nitrogen, oxygen and argon, in water at 0°, and the percentages by volume of these gases in dry air free from carbon dioxide, are given below. The partial pressures are proportional to the volume percentages.

Gas	Percentage by vol	Partial pressure (total = 1 atm.)	Absorption coefficient.
Nitrogen - -	78	0·78	0·0239
Oxygen - -	21	0·21	0·0489
Argon - -	1	0·01	0·053

By multiplying the partial pressures by the absorption coefficients, the volumes of the three gases dissolved in 1 vol. of water saturated with a large volume of air (constant composition) are found to be:

nitrogen, 0·01864; oxygen, 0·01027; argon, 0·00053; sum, 0·02944.

When the dissolved gas is expelled by boiling it will have this composition, or, expressed in percentages by volume it will contain:

$$\text{nitrogen } \frac{1\cdot864}{0\cdot02944} = 63\cdot3, \quad \text{oxygen } \frac{1\cdot027}{0\cdot02944} = 34\cdot9; \quad \text{argon } \frac{0\cdot053}{0\cdot02944} = 1\cdot8.$$

The proportions of oxygen and argon have increased, since these gases are more soluble than nitrogen in water. By shaking water with an

excess of this gas, and expelling the dissolved part, the latter will be still further enriched in oxygen, and so on After eight repetitions the gas will contain over 90 per cent. of oxygen

If the partial pressure of a gas above its solution can 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.

Henry's law does not apply to very soluble gases, such as ammonia at the ordinary temperature, or hydrogen chloride, 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, but with less soluble gases the law holds up to about 10 atm. A few **absorption coefficients** are given below, in vols at S T P , absorbed by 1 vol. of water at the given temperature, 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 -	4 61	3 095	2 635	2 26	1 77	1 41	1 20	1 0
Carbon dioxide -	1 713	1 194	1 019	878	665	53	44	36
Oxygen -	049	038	034	031	026	023	021	0195
Nitrogen -	0239	0196	0179	0164	0138	·0118	0106	0100
Hydrogen -	0215	·0198	0190	0184	0170	0164	0161	0160

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 **partially miscible.** Successive small quantities of ether added to water at first dissolve completely. At a certain point, the water becomes saturated with ether ; 100 gm. of water then take up 5·8 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 4·12 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. 10), 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 - - - -	5 8 gm	4 12 gm
Chloroform - - -	0 62 ,,	0 10 ,,
Carbon disulphide -	0·218 ,,	10 81 ,,

The partition law.—Iodine, when shaken with chloroform and water, dissolves in each solvent, but the chloroform layer, as is seen from the colour, contains most of the iodine Berthelot and Jungfleisch (1872) found that the weights of dissolved substance per unit volume of each liquid were in a constant ratio, independent of the amounts of the dissolved substance or of the liquids. The substance is shared by the two solvents in a constant ratio. This result is called the **distribution, or partition, law.**

If c_1, c_2 are the concentrations, or weights per unit volume, of the solute in the two layers, respectively, then

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

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**, k, is

$$\frac{\text{concentration in carbon tetrachloride}}{\text{concentration in water}} = \frac{4\cdot412}{0\ 0516} = 85\ 5$$

A saturated solution of iodine in water at 25° contains 0·340 gm. per litre. From the partition coefficient we calculate the concentration of a solution of iodine in carbon tetrachloride, in equilibrium with a saturated solution in water, as $0\cdot340 \times 85\cdot5 = 29\cdot1$ 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 can exist in equilibrium with excess of solute under given conditions (*e.g.*, at a fixed temperature) is called a **saturated solution** : salt [solid] ⇌ salt [dissolved].

The **concentration** of a solution 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 characters of solute and solvent, (2) on temperature, and (3) to a slight extent on pressure, in some cases (sodium chloride) increasing, in other cases (ammonium chloride) decreasing, with increase of pressure.

The solubility usually increases with the temperature. In a few 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 1.—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 hot water. In a short time crystals of the salt separate. They redissolve on cooling.

The dependence of solubility on temperature is represented graphically by means of **solubility curves**, in which the abscissae represent temperatures, and the ordinates the solubilities. In Fig. 56 the solubility curves of some salts in water are exhibited. It will be seen that these show a great diversity.

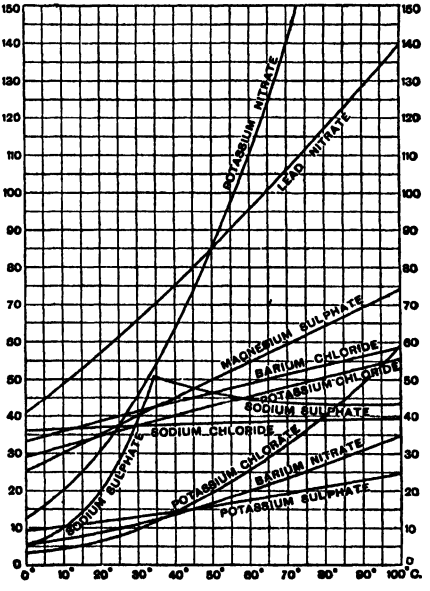


FIG 56.—Solubility curves.

Supersaturation.—In many cases, when a saturated solution is cooled, the dissolved substance is not deposited. The cooled solution then contains more solute than corresponds with saturation at the given temperature, and is said to be **supersaturated**. Crystallisation is induced by throwing a small crystal of the solid into the solution.

EXPT 2.—Heat on a water-bath 250 gm. of crystallised sodium thiosulphate ("hypo") in a 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 supersaturated 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.

EXPT 3 —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. 398)

A supersaturated solution when strongly cooled may crystallise spontaneously, without contact with solid. If a supersaturated solution of hypo is cooled in a freezing mixture, it crystallises spontaneously.

Determination of solubility.—The solubility of a salt at various temperatures is best determined by stirring the powdered solid salt with the solvent 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 4 —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

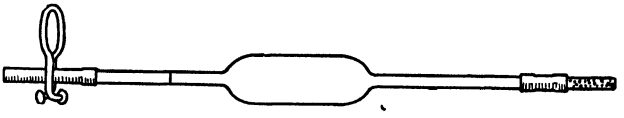


FIG 57 —Pipette for determination of solubility.

piece is connected with a short piece of tubing, packed with glass wool, to serve as a filter (Fig. 57) The pipette is cleaned and dried. A quantity of powdered potassium nitrate is now well 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. After stirring for some minutes the filter is attached to the pipette, and solution drawn into the latter. The filter is detached, the solution run from the pipette into a weighed weighing bottle, the latter stoppered, allowed to cool, and

weighed. The solution is poured into a weighed porcelain dish (And any crystals separating in experiments at higher temperatures are washed from the bottle 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. 56).

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. Calcium sulphate occurs in two forms containing water. One of these is gypsum. If gypsum is heated to 120°–130° it loses part of its water of crystallisation, forming plaster of Paris. This 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 (" set ") to a mass of gypsum.

It will be seen from Fig. 56 that the solubility curves of sodium, potassium and barium 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 calculated as **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	100 (30°)	137 (60°)
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	0 279 (40°)	0 260 (60°)
Strontium sulphate - - -	—	0 0011	—
Barium sulphate - - -	—	0·00023	—
Silver chloride - - - -	—	0 00015	—
,, bromide - - - -	—	0 00001	—
,, iodide - - - - -	—	0 00000035	—

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

Sea water freezes at about −2°; Bishop R. Watson in 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. Freezing serves to separate the constituents of a solution, just as distillation enables us to achieve the same end (p 77). The solution remaining will become increasingly richer in salt as more and more ice separates, and hence the freezing point falls as ice continues to be formed.

A limit is reached when so much solvent has frozen out that the amount remaining in the liquid is only just sufficient to keep the salt in solution. On further cooling, both ice and salt separate together in the same ratio as they exist in the solution, and hence the temperature becomes constant, and the whole of the solution then solidifies without further fall in temperature. 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, 1875). Later experiments 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.**

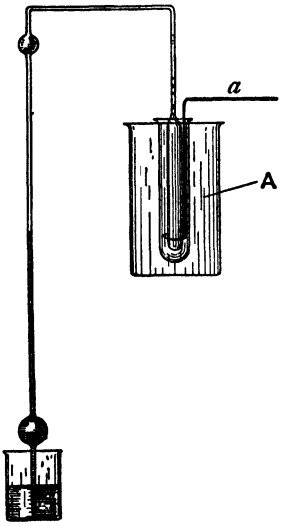


FIG. 58.—Depression of freezing point

EXPT 5.—An air-thermometer bulb is placed in a large test-tube supported in a beaker (Fig 58). The tube of the air thermometer has two bulbs, 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.

Degrees of freedom.—The volume of a given quantity of gas depends on the temperature and pressure, but if any two of the three variables, pressure, volume and temperature, are fixed, the third assumes a definite value Vapours behave similarly, so long as no liquefaction occurs. In the same way the volume of a liquid or solid is fixed at a given temperature and pressure. It is most convenient to consider the **specific volume**, or reciprocal of the density, and we can then say that the **state** of any homogeneous phase (gas, liquid or solid) is completely determined when any *two* of the three variables, pressure, temperature and specific volume, are fixed This system of one phase ($P=1$) is said to possess two **degrees of freedom**, ($F=2$), the number of degrees of freedom for any system being the smallest number of independent variables defining the state of the system which must be given definite values before this state is completely determined.

A pure liquid can exist in equilibrium in contact with its vapour only at one definite pressure (the vapour pressure) at a fixed temperature. The densities of liquid and vapour are then fixed, and the states of both phases (liquid and vapour) are completely determined If the pressure is increased, some vapour condenses until the original pressure is restored , if the pressure is reduced, some liquid evaporates until the same result is attained. The system composed of water and ice behaves similarly : on increasing the pressure, some ice melts and the original pressure is restored. A system composed of two phases of a pure substance has *one* degree of freedom ($F=1$).

Ice, liquid water and water vapour can coexist only at one temperature and one pressure, viz., $+0{\cdot}0077^\circ$ and $4{\cdot}57$ mm · these specify the **triple point** for water, at which three phases coexist ($P=3$) In this case there is no degree of freedom ($F=0$). All the above results apply to pure substances, not to solutions

Vapour pressures of solutions.—Water and its vapour coexist in any proportions at a given temperature, under a fixed pressure, the vapour pressure. In the system composed of two phases of the pure substance in equilibrium: Water [liquid] $\rightleftharpoons$ Water [vapour], there is only one degree of freedom. Now let a little common salt be passed into a barometer tube containing water and water vapour. It dissolves in the water, and the vapour pressure is slightly diminished. By dissolving further quantities of salt, the vapour pressure falls still further. The system composed of two phases, solution and vapour, in equilibrium, shows two degrees of freedom instead of only one, as in the case of pure water. The difference arises from the fact that the liquid phase is no longer a pure substance, 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 until the solution is just saturated with salt. The vapour pressure is again constant, since

further addition of salt has no effect on the concentration, but merely remains as an undissolved solid. The appearance of an extra phase, solid salt, has reduced the number of degrees of freedom by one, since the pressure now depends on a single variable, the temperature. 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, viz., the **concentration.**

To form a system of phases, some or all of which are solutions, or pure substances not convertible into one another, we require a limited number of substances from which *every* phase may be constituted. The *least* number of these is called the **number of components** of the system. Each of the three phases forming the triple point of water can be composed of a single substance, water ; 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) $\rightleftharpoons$ Water (vap)
1	2	1	Water (solid) $\rightleftharpoons$ Water (vap)
1	2	1	Water (solid) $\rightleftharpoons$ Water (liq)
1	3	0	Water (solid) $\rightleftharpoons$ Water (liq) $\rightleftharpoons$ Water (vap)
2	2	2	Salt (dissd) $\rightleftharpoons$ Salt (solid)
2	2	2	Water (in sol) $\rightleftharpoons$ Water (vap)
2	3	1	Water (in sol) $\rightleftharpoons$ Water (vap) Salt (dissd) $\rightleftharpoons$ Salt (solid)

In all cases a simple relation exists between the number of phases, P, of components, C, and of degrees of freedom, F, viz.,

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

$$P + F = C + 2,$$

This relation is perfectly general, and applies to all heterogeneous systems in equilibrium ; it is called the **phase rule** (Willard Gibbs, 1876).

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 $F = 1 + 2 - 1 = 2$.

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 $\rightleftharpoons$ Liquid, or Solid $\rightleftharpoons$ Vapour, or Liquid $\rightleftharpoons$ 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 $\rightleftharpoons$ Liquid $\rightleftharpoons$ 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 $\rightleftharpoons$ Gas (dissd) $P=2$, hence $F=2+2-2=2$, *i e*, temperature and 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 $\rightleftharpoons$ Solid (dissd) · $P=2$, hence $F=2+2-2=2$, *i e*, the solubility depends on temperature and pressure The effect of pressure, which is slight, could have been predicted by the phase rule

(*c*) Solid $\rightleftharpoons$ Solution $\rightleftharpoons$ 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 $\rightleftharpoons$ 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 general, simple, and capable of very extensive application.

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 approximate 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 approximately 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* $P+F=C+2$.

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 Stochiometrie*, or *Rudiments of Stoichiometry* (Breslau, 1792–94), 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.

The Atomic Theory 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*

"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 mensurâ*"

This law was not established 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 Solutions of sulphuric acid, salts, alcohol, etc , and metallic alloys, amalgams and glasses, 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, 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 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 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 these he regarded 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 fourth 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.** 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 simple; 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, sometimes they contain definite compounds of the metals, and sometimes all of these states. Only comparatively recently has the application of the Phase Rule made it possible to decide to which class a particular alloy belongs. Proust was wise in refusing to be in a hurry to answer this question.

The exactness of the law of constant proportions was apparently established by 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 seemed to show that, if such differences existed, they did not exceed 1 part in 100,000, and were within the limits of experimental error

Isomerism and allotropy.—The law of constant proportions asserts that a definite compound has a fixed chemical composition. The converse is not always 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 phenomenon is known as **isomerism**, and different substances of the same composition are called **isomers**. Chemical composition alone does not uniquely determine a pure substance.

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. The name allotropy is now frequently applied to compounds in different physical states, such as the two forms of mercuric iodide, as well as to forms of elements.

Sulphur, on heating, melts to a mobile pale yellow liquid On further heating this is suddenly transformed into an orange-red viscous mass, which darkens as heating is continued, until at 440° it is almost black. The liquid, if then poured into cold water, forms a brownish-yellow transparent elastic mass. On standing for a few days,

this slowly becomes opaque and brittle, it is partly reconverted into ordinary sulphur, but another allotropic form is also present.

Isotopes.—The unique composition of a pure substance, apparently established by Stas, is now known to be approximate only. Soddy and Hyman in 1914 found that specimens of lead chloride, prepared respectively from thorium and uranium minerals containing lead, differed in composition by 1 part in 225, although identical in chemical properties. This 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 makes the question of the combining ratios of elements, and the definition of an element, much more difficult than was formerly supposed.

Some results giving the weights of different specimens of lead, from minerals, which combine with 70·92 parts of chlorine, are given in the table below. The first three minerals are all varieties of pitchblende, uranium minerals free from thorium; the last two are thorium minerals containing also some uranium. The value for ordinary lead is 207 2.

East African pitchblende	206·05
Broggerite	206 06
Clèveite	206 08
Thorianite (containing also 26·8 per cent uranium)	206·83
Thorite (30 1 per cent thorium, 0·45 per cent uranium)	207 90

It will be explained later how it has been possible to prove that many ordinary elements are mixtures of isotopes The facts that these mixtures are inseparable by ordinary chemical means, and that all specimens of the element contain the isotopes in the same ratios, cause the element to appear in all chemical changes as a single substance, so that although Stas was undoubtedly dealing with mixtures in what he considered pure elements, he was unable to discover this The same applies to all ordinary chemical processes It is only by very special methods that isotopes can be separated, although in one or two cases, as in the natural varieties of lead formed in radioactive changes, different natural specimens of an element have different combining proportions Ordinary chlorine is a mixture of two isotopes, sodium is a single unmixed element, yet all specimens of common salt so far examined have been identical in composition, the isotopes of chlorine present in them being always mixed in the same ratio

The law of multiple proportions.—As a result of 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: *when 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 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*. In the two oxides of tin (p 92), the weights of tin combining with 100 parts of oxygen are in the ratio 1 : 1·87. According to Dalton, the ratio should be exactly 1 : 2. Dalton's analyses were no more exact than the former, but those subsequently made by Berzelius established the accuracy of the law.

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 carbon by Desormes, and of two hydrides of carbon by Dalton (1804), the latter results probably rounded off, also confirmed the law :

	Carbon monoxide	Carbon dioxide
Carbon	44	28 1 or 44
Oxygen	56	71 9 or 112 6 = 56 × 2 01
	Marsh gas.	**Olefiant gas**
Carbon	4·3	4·3
Hydrogen	2	1

A striking example of the law of multiple proportions is provided by the five oxides of nitrogen. The weights of oxygen combined with 100 parts of nitrogen in these 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

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

EXPT 1 —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. The mixture is converted into a *green* powder (**mercurous iodide**). To this add a further 6·35 gm. of iodine, and triturate. The 10 gm. of mercury and 12·7 gm. of iodine give a *reddish-yellow* powder (**mercuric iodide**). In mercuric iodide the same weight of mercury is combined with *twice* the amount of iodine contained in mercurous iodide.

EXPT. 2.—Wrap 0·1 gm. of bicarbonate of potash in tissue paper and pass it to the top of a eudiometer filled with mercury, the upper part containing 1 c.c. of concentrated hydrochloric acid. Carbon dioxide is evolved. Heat gently 0·2 gm. of bicarbonate in a crucible for a few minutes: it loses some carbon dioxide, forming carbonate of potash. If this is treated with acid, it evolves exactly the same volume of gas as the 0·1 gm. of bicarbonate. Hence the bicarbonate, on heating, loses exactly half its carbon dioxide in forming the carbonate.

Experiment 2 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 ratios 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 was illustrated by Stas (1849). Carbon dioxide was prepared by passing oxygen over a weighed amount of pure charcoal, diamond, or graphite, heated in a tube, and the gas was absorbed 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 contained 27·278 parts of carbon. The weight of carbon monoxide yielding 100 parts of carbon dioxide was 63·640. Hence, 100 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.

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 decompose 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. In some experiments which he did not publish Cavendish

weighed out equivalent weights of salts, dissolved them in equal volumes of water, and compared the electrical conductivities of the solutions.

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 Korper* (*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 anaysis 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*.

Now $\frac{1}{2}$ oz of *luna cornea* contains $53\frac{7}{16}$ grains of " Salzsaure " (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 $159\frac{3}{5}$ 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 *Stoichiometry*, 1792–4. Richter's reasoning is quite unnecessarily obscured by attempts to derive mathematical relationships where Nature has not provided any; stripped of its verbiage, and exhibited in 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

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

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 **equivalents**, of the elements, are 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. 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.*

When 23 gm. of sodium are heated in hydrogen chloride gas, 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, in the first instance, as the standard element, 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 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. 57) 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. It is only rarely, however, that oxides can be obtained sufficiently pure for the exact determination of equivalents ; chlorides or bromides are more often used

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 an 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 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 by repeated evaporation with nitric acid From the known equivalents of potassium chloride and oxygen, the equivalent of nitrogen is calculated

Elements which combine in more than one proportion have more than one equivalent. The law of multiple proportions then shows that the different equivalents of an element are related in simple multiples. Carbon forms two compounds with oxygen, containing, for 7·94 parts of oxygen, 2·978 and 2·978 × 2 parts of carbon, respectively (p. 96).

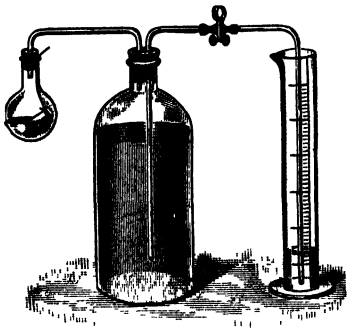


FIG. 59.—Apparatus for determination of equivalents.

In determining the equivalent of a metal which dissolves in acids or alkalies with evolution of hydrogen, the apparatus shown in Fig 59 may be used About 1 gram of the metal is weighed into the small tube, which is carefully placed in the small flask containing the acid or alkali in solution. The apparatus is then fitted together, the bottle being filled with water, and the clip opened. By shaking the metal is brought into the liquid, and the hydrogen evolved displaces water into the cylinder. After the action has ceased, and the temperature has again become that of the room, the water levels are adjusted and the volume read off. This is reduced to S T P. and the weight of hydrogen calculated By dividing the weight of metal by the weight of hydrogen the equivalent of the metal is found. In this way zinc, magnesium, iron and calcium may be dissolved in cold dilute hydrochloric acid, tin in hot concentrated hydrochloric acid,

and aluminium in a mixture of equal volumes of concentrated hydrochloric acid and water or in warm dilute caustic soda solution.

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 were accepted for a number of years as the most accurate values.

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, according to Stas, not certainly known, he 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

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

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

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

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

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

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

In 1895 Morley determined the ratio *hydrogen/oxygen* with great care and found 1 : 7·9395 ; Scott (1893), and Burt and Edgar (1916), in most accurate researches, found 1 : 7·938. The equivalent of chlorine was determined, with reference to hydrogen, by a determination of the density of hydrogen chloride gas, and the decomposition of the latter by heated aluminium, with liberation of hydrogen (Gray and Burt, 1909). The equivalent of chlorine, 35·187 (H = 1) referred to oxygen = 8·000 is thus

$$35{\cdot}187 \times 8{\cdot}000 \div 7{\cdot}938 = 35{\cdot}458,$$

which differs from Stas's figure by as much as 1 in 1500.

This discrepancy, confirmed by other modern atomic weight 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 carried down some of the latter salt, which cannot be completely removed by washing.

The modern equivalents of the majority of the important elements are based on the equivalents of silver, chlorine or bromine. Oxygen appears in few direct ratios, and practically no oxides are suitable for exact analysis. Of the fundamental secondary standards bromine forms a most unstable oxide, the oxides of chlorine are explosive and difficult to prepare in a state of purity, and silver cannot be referred directly to oxygen, since the oxide cannot be obtained sufficiently pure On the oxygen standard the value for nitrogen was involved as an intermediate link, from the ratio *silver/silver nitrate*

T. W Richards, of Harvard, on whom the mantle of Stas had fallen, prepared silver nitrate from pure silver and found that, if the combining weight of nitrogen is to be taken as 14·008, as the physical methods of gas densities indicate, then that of silver must be 107 880 He was at first not inclined to alter Stas's figure, 107 93, but since the rejection of the newer figure for nitrogen was clearly impossible in the face of several confirmatory researches, Richards fixed silver arbitrarily as 107 880, and took this as the basis of his figures Attempts to obtain a direct value of the ratio *silver/oxygen*, by the roundabout method of converting lithium chloride into perchlorate by evaporation with perchloric acid, and also precipitating lithium chloride with silver nitrate, failed to give Richards and his pupils any certain result, and a laborious series of experiments on silver oxide by H B Baker and H. L. Riley (1926) gave the low value of 107·86 for silver, apparently because this oxide could not be obtained in a state of complete purity Moles and Clavera (1927), by a very accurate determination of the limiting density (p 121) of nitrogen, found the combining weight 14 0082 ± 0 00004, which requires silver to be 107 880 Although a new determination of the ratio *silver/silver nitrate* by Hönigschmidt (1927) gave 107·879, Honigschmidt and Sachleben (1929), by heating barium perchlorate to give oxygen and barium chloride, and then precipitating silver chloride from this by a silver salt, were able to calculate a ratio *silver/oxygen* which gave 107·880 for the combining weight of silver.

The existence of three isotopes (16, 17 and 18) in ordinary oxygen makes the " chemical " atomic weights, determined with respect to O = 16 000, really about 2 parts in 10,000 higher than those determined (say by the mass spectrograph) by " physical " methods, which are referred to the isotope $O^{16} = 16\ 000$ (Aston, *J. Chem. Soc.*, 1932, p. 2890).

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.

The existence of **isotopes** complicates the definition of an element and the statement of the law of constant proportions.

CHAPTER VIII

THE ATOMIC THEORY

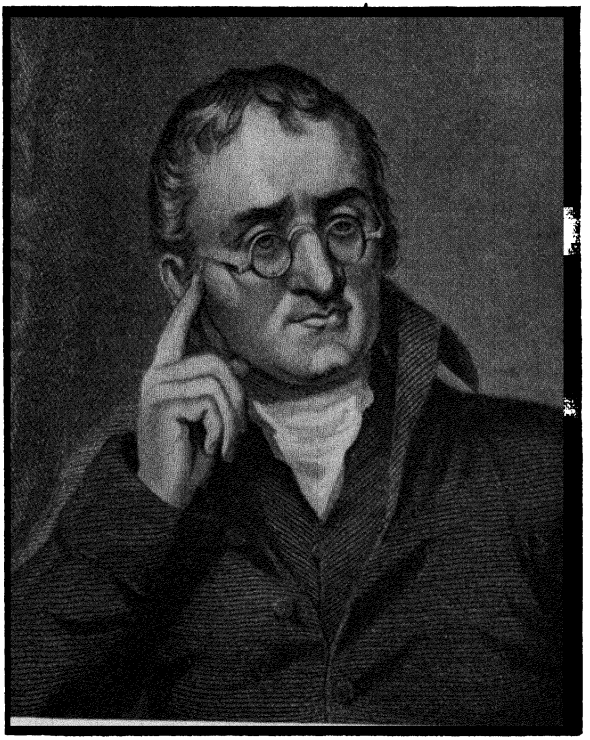
Atoms.—The laws of chemical combination, particularly the law of multiple proportions, suggest that the chemical elements react together as though the matter of which they are composed is parcelled out into exceedingly minute portions, each incapable of further subdivision, so that when two elements combine they do so in masses which are whole multiples of the masses of these indivisible portions. This is a **hypothesis** as to the **structure of matter.** We are not, of course, able to see these minute particles even with the most powerful microscopes (see p 6) We shall find, 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 present themselves. The first sees matter as a continuous structure, completely filling the space occupied by bodies in the same way as jelly fills a mould. The second sees matter filling space discontinuously, with interstitial gaps, much as small shot fills a barrel The first view is associated with the Eleatic school of Greek philosophy, founded by Xenophanes (576–480 B.C.); the second is the **atomic hypothesis,** due to Leukippos (*c.* 500 B.C.), but particularly developed by Demokritos of Abdera (*c.* 450 B.C.). This assumes the division of matter into exceedingly small particles, or **atoms,** incapable of further division by physical means.

The atomic hypothesis, therefore, appears to have originated in Greece about 500 B.C. and to have been proposed by Leukippos. It is uncertain whether it was independently proposed in India, but it certainly appears there in a novel form in later Buddhist and Jainist treatises. The idea of divisible atoms (*i.e.*, molecules) was put forward by Asklepiades of Prusa (100 B.C.).

Epicurus (340 B.C.) and Lucretius (57 B.C.) adopted the theory, and we possess a long Latin poem of the latter, *De Rerum Natura*, dealing principally with the atomic theory. Van Helmont, Lemery (1675), Boerhaave (1724), Boyle, and Newton (1642–1727) made use of the hypothesis; the last, although the author of the dictum ***hypotheses non fingo***, was a thoroughgoing atomist. Newton gave a mathe-

matical 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, centres of attractive and repulsive forces, and endowed with mass.



JOHN DALTON.

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** 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).

The origin of Dalton's atomic theory.—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 Apart from this it is difficult to say what led Dalton to his 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 formerly accepted 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. 95) But the analyses of these gases were not made until 1804, whereas the first list of atomic weights appeared in 1803 (3) Dalton's notes of lectures, given at the Royal Institution in 1810, trace the theory of 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 probable that Dalton was led to the 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

The atomic theory.—The atomic theory of Dalton, the great guiding principle of modern chemistry, is so simple that, as Lothar Meyer has said, "at first sight it is not illuminating."

The chemical elements are assumed to consist of very minute particles of matter, **atoms**, which preserve their individuality in chemical changes. Dalton was firmly convinced that atoms are indivisible; he said: "Thou knowest thou canst not cut an atom," and when referred to the sesquioxides, which apparently contain 1½ 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.

In the modern theory the nuclei of atoms (p. 6) which contain all but a small part of the material of the atom, enter and leave chemical changes unaffected, but some of the outer electrons are removed or redistributed. This part of Dalton's theory is, therefore, essentially retained.

Dalton assumed that all atoms of the same element are identical in all respects, particularly in weight or mass. Different elements have atoms differing in weight. Each element is characterised by the weight of its atom.

Dalton's second assumption has been considerably modified by the discovery of isotopes, and can no longer be maintained One element, *e g*, chlorine, may have atoms differing in mass, and the atoms of such an element are not necessarily all the same, since the ordinary element may be a mixture of isotopes It is not, therefore, the mass of its atom, the **atomic weight,** which characterises an element, modern theory teaches that this part is played by the net positive charge on the nucleus of the atom, the so-called **atomic number.** All isotopes have the same atomic number, although they may have different atomic masses The "element lead" is any one of the ten different isotopes of lead, or mixtures of any or all of them in any proportions

The **absolute weights of atoms,** as Dalton realised, are very small indeed; 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 is 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 to be $1{\cdot}66 \times 10^{-24}$ gm. Thus, 1 cm.^{3} 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 $236 \times 1{\cdot}66 \times 10^{-24} = 3{\cdot}92 \times 10^{-22}$ gm.

Chemical combination, according to Dalton, occurs by the union of the atoms of the elements in whole 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").

Deduction of the laws of stoichiometry.—Since 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** (p. 14). It applies, strictly speaking, to the atomic nuclei.

The **law of constant proportions**, and its apparent exceptions, are explained by the atomic theory. A compound is composed of molecules made up of atoms of the constituent elements in fixed ratios and therefore has a constant composition if the atoms of each element are all of the same kind, or consist of an unvarying mixture of isotopes. The composition of a compound will be variable when it is formed from different isotopes or different mixtures of these. If the ordinary element is an inseparable mixture of isotopes, its compounds with another element similarly constituted, or with a simple element, will be unvarying in composition, since the mixtures of isotopic atoms always enter into combination as wholes and are never separated into parts by such changes In all cases the composition expressed in numbers of atoms per molecule remains the same.

If two elements combine in more than one proportion, the molecule of one compound may be formed by adding a whole number of atoms of one or both elements to one or more molecules of the other compound. This explains the **Law of Multiple Proportions.**

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 be either the atomic weight itself, or a simple fraction of it, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}$, 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 case is the equivalent greater than the atomic weight, viz., 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.—Dalton's theory provided no means of determining even the relative weights of the atoms. 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 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 Davy supposed from the combining volume ratio, 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 :

$$Q_1 \cdot Q_2 = a_1 A_1 : a_2 A_2,$$

where A_1 and A_2 are the atomic weights, and a_1, a_2 are the whole numbers of atoms of each element which enter into combination.

$Q_1 : Q_2$ alone does not enable us to find the ratio of the atomic weights, unless the ratio $a_1 : a_2$ is also known.

Dalton was compelled to use **empirical rules**, which he recognised as arbitrary. He assumed that, if only one compound of two elements is known, it is formed of one atom of each element. 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 two atoms of the same element repel each other, and do not usually form a stable compound with a third atom. This reasoning had been used 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.

The work of Berzelius, who extended Dalton's investigations with great enthusiasm and success, led to improvement in this respect, since his skilful use of chemical analogies, of the law of gaseous volumes, of atomic heat and of isomorphism, led to values for atomic weights which are those now adopted, with only a few exceptions, *e.g.*, for the alkali metals and silver, Berzelius's later atomic weights were double the modern values. Many chemists, such as Davy and Wollaston, preferred to use equivalent weights as being independent of hypotheses and Leopold Gmelin, in his large *Handbook* (1817–19; English translation, 19 vols, 1848–72), used equivalents. In other quarters an intolerable diversity arose, dictated almost entirely by authority, and the atomic theory appeared to have outgrown its usefulness.

Dalton's assumption that the particles of elements in the free state are single atoms was the main source of the difficulties of the earlier theory. The true theory, that the molecules of elements may contain more than one atom, which would have resolved the growing difficulties, was given by the Italian physicist Avogadro in 1811, but was entirely unheeded until it was revived in 1858 by his countryman, Cannizzaro.

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 metals with the planets appears in Babylonian texts of 1600 B.C., but was first systematised in the Neo-Platonic theories of "sympathy" (*c.* 100 A.D.), and led to the alchemical names and symbols:

Gold (yellow) was called **Sol** (the Sun) and represented by ☉; Silver (white) was named **Luna** (the Moon), ☾; Copper was named after **Venus**, ♀; Tin was **Jupiter** ♃; Iron was named after **Mars**, ♂; **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 (384–322 B C) The name mercury still survives, and silver nitrate is often called *lunar caustic*. Gold, silver, copper and iron were known to the Predynastic Egyptians (before 3400 B C).

The **nomenclature of the alchemists** was purely empirical The same substance had a variety of names, depending on its mode of preparation, and names were often based on accidental resemblances Thus *butter of antimony* was classed with ordinary butter, and *oil of vitriol* (sulphuric acid) with olive oil

A **scientific nomenclature** began with Macquer and Baumé, who, for example, classed together the glassy, crystalline substances *white vitriol* (zinc sulphate), *green vitriol* (ferrous sulphate), and *blue vitriol* (copper sulphate) Bergman's system of nomenclature (1782) 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 metals have names ending in **-um** and non-metals in **-on.** Many elements have names derived from Greek roots: *e g.*, **chlorine**, from χλωρός, *chloros*, greenish-yellow; **chromium**, from χρῶμα, *chroma*, colour. 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 (in Sweden), **hafnium**, from Copenhagen; **masurium**, after lakes in East Prussia, and **rhenium**, from the Rhine. **Beryllium** and **zirconium** are named after the minerals, *beryl* and *zircon*, which contain them, **palladium** and **uranium** 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 an extension by Berzelius (1813) of a system used by Thomson (1802): it replaced Dalton's inconvenient circular symbols by the initial letter, or the initial and one other letter, of the Latin name. The **symbol** has a quantitative significance, and represents one **atom**, or one **atomic weight**, of the element. O represents 16 parts by weight of

oxygen ; Cl represents 35·5 parts by weight of chlorine. This is the most important feature of the system of chemical notation.

The symbol W, given to tungsten, is from the German name *wolfram* The 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 and formulae of compounds.—The names of compounds indicate their composition. In the names of compounds of two elements, the name of the more electropositive (p 415) element 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

The formulae of compounds are made up 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 compound, unity being always understood.

Since two elements may combine in more than one proportion, this is represented in the nomenclature in one of two ways : (1) by suffixes, added to the Latin names ; (2) by prefixes :

Cu_2O, cuprous oxide CuO, cupric oxide	Suffixes	SO_2, sulphur dioxide SO_3, sulphur trioxide	Prefixes

The suffix **-ous** denotes the *lower*, and **-ic** the *higher*, proportion of an element, respectively. The prefixes **sub-**, **proto-**, and **sesqui-** have practically gone out of use.

In a series of oxides, the one containing the *highest* proportion of oxygen is sometimes called a **peroxide**, but it has been proposed to restrict this name to a special class of oxides, giving hydrogen peroxide (H_2O_2) with acids, such as Na_2O_2, BaO_2. The name peroxide is used rather loosely.

A chemical change is represented by an **equation**, which indicates how many molecules of the initial substances interact to produce the specified number of molecules of the products. The numbers of atoms

of every element must be the same on both sides of the equation, that is, the latter must be *balanced.*

Acids, bases, and salts.—The most important compounds of three elements 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.

Sulphur**ous** acid, H_2SO_3	Sodium sulph**ite**, Na_2SO_3
Sulphur**ic** acid, H_2SO_4	Cupr**ic** sulph**ate**, $CuSO_4$.

If an element forms more than two oxy-acids, the prefixes **hypo-** (*below*) and **per-** (*above*) are used :

Hyposulphur**ous** acid, $H_2S_2O_4$	Sodium **hypo**sulph**ite**, $Na_2S_2O_4$.
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** (*a* without ; ὕδωρ (*hudor*) water) : P_2O_3, phosphor**ous** anhydride (note that the element is phosphor**us**) ; P_2O_5, phosphor**ic** anhydride

By the combination of acidic oxides with water, **acids** are produced :

$$SO_3 + H_2O = H_2SO_4 \text{ (sulphuric acid).}$$

Oxides of metals yielding **bases** (alkalies or alkaline earths) with water are called **basic oxides.**

Common bases in aqueous solutions 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 so-called alkali-metals are called **alkalies** ; those of calcium, strontium, and barium are called **alkaline earths :**

$$K_2O + H_2O = 2KOH \text{ (potassium hydroxide ; } \textit{caustic potash}).$$
$$CaO + H_2O = Ca(OH)_2 \text{ (calcium hydroxide, } \textit{slaked lime})$$

Acidic and basic oxides *combine* to form **salts** :

$$SO_3 + Na_2O = Na_2SO_4 \text{ (sodium sulphate).}$$

Acids and bases *interact* to produce salts, but water is formed at the same time ·

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O.$$

The salt Na_2SO_4 may be regarded as sulphuric acid in which two atoms of hydrogen are replaced by two atoms of sodium, and acids may be considered as **salts of hydrogen,** which can be displaced by metals.

$$Zn + H_2SO_4 = ZnSO_4 \text{ (zinc sulphate)} + H_2.$$

Metals can also replace hydrogen in bases or other hydrogen compounds :

$$Zn + 2KOH = K_2ZnO_2 + H_2.$$
$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

Salts are formed (i) by the union of acidic and basic oxides ; (ii) by the action of acids on hydroxides or oxides ; (iii) by the action of acids on carbonates (when carbon dioxide is evolved with effervescence) or other salts of volatile acids ; (iv) by the interaction of other salts.

$$SO_3 + BaO = BaSO_4 ;$$
$$H_2SO_4 + 2KOH = K_2SO_4 + H_2O ;$$
$$H_2SO_4 + CuO = CuSO_4 + H_2O ,$$
$$2HCl + CaCO_3 = CaCl_2 + H_2O + CO_2 ;$$
$$H_2SO_4 + KNO_3 = KHSO_4 + HNO_3 ,$$
$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2KNO_3 ;$$
$$NH_3 + HCl = NH_4Cl \text{ (a special type of salt formation).}$$

Radicals.—In certain compounds a **group of atoms** plays the part of a single atom, and occurs in a whole series of compounds 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**, and in all sulphates the radical SO_4 is present .

$$NH_3 + HCl = NH_4Cl, \text{ ammonium chloride}$$
$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4, \text{ ammonium sulphate.}$$

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.

SUMMARY OF CHAPTER VIII

The laws of stoichiometry are explained by the **atomic theory.** This supposes that (1) all matter is made up of minute particles, called **atoms**; (2) some elements contain atoms of one kind only, others are mixtures, usually in unvarying proportions, of different kinds of atoms called **isotopes** of the element, which enter into chemical changes without separation , (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; (4) each kind of atom has a definite small weight or mass , those of isotopes are different.

The absolute mass of the lightest atom, 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 a standard atom is called the **atomic weight.** The atomic weight of oxygen is taken as 16 000, and hydrogen is then 1 0077. Each element has a **symbol,** denoting one atomic weight. The **formula** of a compound denotes one molecular weight.

CHAPTER IX

AVOGADRO'S HYPOTHESIS AND THE MOLECULE

The law of gaseous volumes.—The relative combining volumes of hydrogen and oxygen 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 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.

1 volume of oxygen combines with 2 volumes of hydrogen to give 2 volumes of steam.

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. 121) 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 from Boyle's law.

Dalton seems to have assumed that the results of Gay-Lussac required that equal volumes of elementary gases contain equal numbers of atoms and he had previously rejected this assumption. In the first place, Dalton's own (inexact) measurements of combining volumes did not confirm Gay-Lussac's law : 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 is lighter than oxygen, whereas the ultimate particle of steam must be heavier than that of oxygen, since it contains the latter.

A 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 should contain only half as many particles in a given volume as nitrogen or oxygen.

Avogadro's hypothesis.—Avogadro in 1811 resolved the difficulty. He 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 independent existence.*

Maxwell defined a molecule of a gas 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* The molecule of a substance may be different under different conditions The molecule of iodine vapour at temperatures below 700° consists of two atoms, I_2 At higher temperatures an increasing fraction of I_2 molecules is decomposed into single atoms of iodine, $I_2 = 2I$, and in this case the atom is identical with the molecule In many solid salts, it is believed that the crystal is formed of a regular aggregate of electrically charged atoms, or **ions**; in common salt, for example, the molecule NaCl is not present as an individual in the solid, which consists of an aggregate of charged sodium and chlorine ions, Na^+ and Cl^-, arranged in a cubical packing In solution in water, also, common salt is largely, if not entirely, present as sodium and chlorine ions (p 260), not as NaCl molecules. In the state of vapour the molecules NaCl are present In liquid water there appear to be molecules more complex than H_2O, which is present in steam, *i.e.*, $(H_2O)_n$ molecules. The definition of the molecule in any particular state follows from the determination of the **molecular weight**, as will be explained in due course, and a particular material may contain several kinds of molecules, *e g*, I_2, I in iodine vapour.

Molecules of gases.—The difficulty which had confronted Dalton could now be removed. Avogadro pointed out that *the molecules of elementary gases are not necessarily the atoms themselves, but usually consist of groups of atoms.* Both kinds of particles, atoms and molecules, had been called "atoms" by Dalton, but they were really different.

Chlorine and hydrogen combine in equal volumes to form a volume of hydrogen chloride 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 $2n$ molecules, of which n are of hydrogen, and n are of chlorine. After combination, the 2 volumes of hydrogen chloride must, by hypothesis, also contain $2n$ molecules. Now each of these molecules must contain at least one atom each of chlorine and hydrogen, hence there must be at least $2n$ atoms of each element present. Thus, the n molecules of chlorine gas, and the n molecules of hydrogen gas, must each have contained $2n$ atoms; in other words, a molecule of each 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, at the same temperature and pressure, are represented by squares or rectangles, and the molecules by small circles. They were used by Gaudin in 1833, with a correct explanation based on Avogadro's hypothesis, and the suggestion that mercury vapour is monatomic, based on its density. Gaudin's memoir seems to have been entirely ignored.

It must be emphasised that Avogadro's hypothesis does not assert that the volumes of the actual *molecules* themselves are equal, but only volumes of *gases* which contain equal numbers of molecules. The compressibility of gases, and the relatively small volumes to which they are reduced by liquefaction, show that there are large spaces between the gas molecules, and the different volumes of liquid obtained from equal volumes of different gases indicate that the actual molecules of different gases have different sizes.

EXAMPLE 1.—**Combination of hydrogen and oxygen** (Fig 60) —2 volumes of hydrogen + 1 volume of oxygen = 2 volumes of steam.

$\therefore$ $2n$ molecules of hydrogen + n molecules of oxygen = $2n$ molecules of steam.

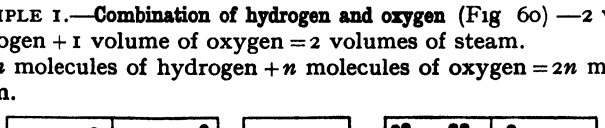


FIG 60.—Combination of hydrogen and oxygen.

"It is necessary and sufficient," said Gaudin, "that the oxygen molecule shall divide into two and that each half shall unite with a

diatomic molecule of hydrogen, therefore oxygen gas is diatomic and water vapour triatomic "

EXAMPLE 2 —**Combination of hydrogen and chlorine** (Fig. 61).—1 volume of hydrogen + 1 volume of chlorine = 2 volumes of hydrochloric acid.

$\therefore$ n molecules of hydrogen + n molecules of chlorine = 2 n molecules of hydrochloric acid.

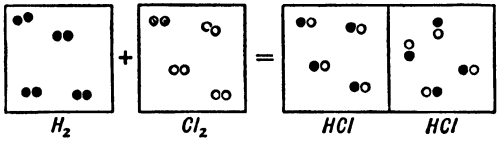


FIG 61 —Combination of hydrogen and chlorine

" It is necessary and sufficient that each combining molecule is divided into two (parts), which we take for atoms Therefore hydrogen, chlorine and hydrochloric acid gases are at least diatomic."

EXAMPLE 3 —**The combustion of carbon in oxygen to form carbon dioxide** (Fig 62).—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 " One volume of carbonic acid contains one volume of oxygen, and therefore one molecule of carbonic acid contains (one molecule or) two atoms of oxygen " 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 the same result is obtained if we assume that n atoms of carbon combine with 2 atoms of oxygen The only result which may be deduced directly is that a molecule of carbon dioxide contains a molecule (2 atoms) of oxygen

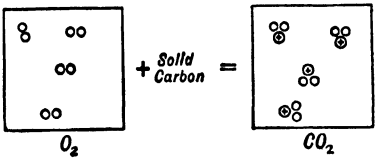


FIG 62 —Diagram illustrating combination of carbon and oxygen.

Molecular weight and relative density.—The molecular weights of substances which exist in the gaseous state, or can be converted into vapour, may be compared by finding the ratio of the densities :

$$\frac{\text{Mol. wt. of substance}}{\text{Mol. wt. of standard}} = \frac{\text{Wt. of any volume of substance}}{\text{Wt. of equal volume of standard}}$$

by Avogadro's hypothesis, the temperature and pressure being the same.

The expression on the right is, however, the relative (or vapour)

density, if the standard substance is hydrogen (p. 60), and since the molecule of hydrogen has previously been shown to contain two atoms, its molecular weight is 2, if H = 1 is the standard of atomic weights. Hence

molecular weight = 2 × vapour density.

To convert the molecular weight so found (H = 1) to the value with oxygen = 16·000 as standard, it must be multiplied by 1·0077, this being the atomic weight of hydrogen on that standard If the relative density is referred to air = 1, then the factor (for O = 16) is 28 98 (p. 62).

Determination of atomic weight from gas or vapour densities.— Avogadro had not clearly stated that molecular weights must be referred to the *atom*, not the molecule, of hydrogen as standard. This important step was taken in 1858 by Cannizzaro, who 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 analyses, the weights of the particular element contained in the molecular weights of the various compounds are found 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 smallest 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 must be 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 will contain only one atom of the element in a molecule.

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 × 2
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
Nitrous oxide	22	44	16
Nitric oxide	15	30	16

The smallest weight of oxygen contained in a molecular weight of any of these compounds is 16, and this is taken as the atomic weight. A molecule of water contains one atom of oxygen, weight 16, and therefore $18-16=2$ parts, or two atoms, of hydrogen The formula of water is therefore H_2O. In this way, Dalton's problem of finding the number of atoms of the elements in the molecule of a compound is easily solved.

CARBON COMPOUNDS.

Compound.	Rel Density $(H=1)\Delta$	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. In 78 parts of benzene there are 72 parts, or 6 atoms, of carbon and $78-72=6$ parts, or 6 atoms, of hydrogen The formula of benzene is C_6H_6.

The molecular weights found from the relative densities are *approximate*, since the vapours do not accurately obey the gas laws, and the determinations are usually approximate. The *accurate* values of the atomic and molecular weights are found from the refined chemical analyses of the compounds, and the vapour density measurements are used simply to decide between various possible molecular weights

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 should agree with this particular multiple. These methods will be considered in more detail later; a brief summary only is given here.

1. Molecular weights of substances in solution, found by osmotic pressure, freezing point, boiling point or vapour pressure methods, usually agree with those found from vapour densities. In some cases, *e g*, metals in amalgams, the molecular weight is identical with the atomic weight

2. The ratio of the specific heats of a gas or vapour at constant

pressure, c_p, and at constant volume, c_v, viz c_p/c_v, has according to the kinetic theory (p. 228), the value 1 667 when the molecule is monatomic. In 1876 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, in the present case, is equal to the atomic weight If the atomic weight found by the vapour density method is shown in one case, viz , mercury, to be the real atomic weight, and not a multiple, it may reasonably be assumed that in other cases also the method gives the real atomic weights

3 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 does not give correct results with elements of small atomic weight

4. Mitscherlich in 1819 found that compounds having analogous formulae 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 from its composition 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

5 The formulae of compounds which show undoubted similarities in chemical properties are usually similar. Oxides of iron, aluminium, and chromium are given similar formulae, 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 be determined This method is the least trustworthy of all Beryllium oxide is similar in practically all its chemical properties to aluminium oxide, but has the formula BeO.

6 The position of the element in the Periodic system (Chap XXIV) is a 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.

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, Em, I, Cl(?), B_1.
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.—The ratio of the **normal densities** of two gases cannot give an exact ratio of the molecular weights For, even if equal volumes contained accurately equal numbers of molecules at one particular pressure, they would, on account of the 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, which result from the deviations from Boyle's law, become less as the pressure becomes smaller, and appear 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** ($p \to 0$), will give the exact ratio of the molecular weights (D Berthelot, 1899)

If W gm of gas at 0° occupy v litres under a pressure p atm , the quotient W/pv is the *density per unit pressure* Boyle's law would make this the same at all pressures, since $pv = \text{const}$ Owing to deviations from Boyle's law, the quotient depends on the pressure If $p = 1$, we have the normal density, if $p \to 0$ the quotient approaches the value for an ideal gas, which is called the limiting density. The ratio of the limiting densities is the ratio of the molecular weights

$$M_a \quad M_b = \frac{W_a}{(p_0v_0)_a} \quad \frac{W_b}{(p_0v_0)_b},$$

where p_0v_0 is the limiting value of pv as $p \to 0$

D, the normal density, is W/p_1v_1, where p_1v_1 is the value of pv for $p = 1$,

$$\therefore \text{ limiting density} = \text{normal density} \times \left(\frac{p_1v_1}{p_0v_0}\right)$$

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 , $(p_0v_0 - pv)/pv$, the relative deviation from Boyle's law, may be assumed proportional to the pressure

$$(p_0v_0 - pv)/p \times pv = \text{const} = \lambda.$$

The compressibility coefficient, λ, may be found from two measurements of pv between 1 atm. and zero pressure then $p_0v_0 = p_1v_1(1 + \lambda)$, since $p_1 = 1$, *i e* ,

$$\text{limiting density} = \frac{\text{normal density}}{1 + \lambda}.$$

(ii) From several 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 the limiting density is then found by multiplying the normal density by (p_1v_1/p_0v_0)

EXAMPLE 1.—The atomic weight of oxygen from the relative density.

	Normal Density.	Compressibility $= \lambda$.
Hydrogen - -	0 089873	−0 00054
Oxygen - -	1·42900	+0 000964

$$\text{Limiting density of hydrogen} = 0{\cdot}089873 \times \frac{1}{1 - 0{\cdot}00054} = 0{\cdot}089922 \text{ gm./lit.}$$

$$\text{Limiting density of oxygen} = 1{\cdot}42900 \times \frac{1}{1 + 0{\cdot}000964} = 1{\cdot}42762 \text{ gm./lit.}$$

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 42762/0 089922 = 15 876

The number found by direct synthesis of water (p 57) 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	54803	55213 (extrapolated).

Limiting density of HCl = 1 63915 × 54803/55213 = 1 62698
Molecular weight of HCl = 2 × 1 62698/0 089922 = 36 186
At weight of Cl (H = 1) = 36 186 − 1 = 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

$$\frac{1{\cdot}63915}{0\ 089873} \times \frac{2}{1\ 00790} = 36\ 191,$$

agreeing to about 1 part in 10,000 with the value from the limiting density

The method of limiting densities gives results at least as accurate as those found by chemical methods, and in some cases greater accuracy is attained

Gram-molecular volume.—The molecular weight in grams of any substance is called the **gram-molecular weight,** or **mol.** In the case of gases, Avogadro's hypothesis shows that at a given temperature and pressure the gram-molecular, or molar, weight will occupy a constant volume. At S.T.P. (0° and 760 mm.) this is called the **gram-molecular volume,** or the **molar volume.** It is the same for all gases in the ideal state, and is **22·415 litres.**

The gas constant.—The general equation for an ideal gas is: pv/T = constant. For a mol of an ideal gas at S.T P . p = 1 atm., v = 22·415 litres, T = 273·09 ; ∴ the value of the constant in the above equation is 22·415/273·09 = **0·08208** litre atmospheres. This is called the **gas constant,** and denoted by R. The **general gas equation,** for a mol of *any* ideal gas, is : $pv/T = R$, or $pv = RT$, where R = 0·08208 if p is in atm., v in litres, and T is the absolute temperature Centigrade.

For any arbitrary weight of gas, W gm., the number of mols is $n = W/M$, where M is the molecular weight. If the volume is V, the molar volume is V/n Hence, in general :

$$pV = nRT \text{ for } n \text{ mols of gas.}$$

It is important to remember that $pv = RT$, *with the value of R stated,* applies only to *one mol* of gas. In general calculations $pV = nRT$ must be used. *E.g.*, to find the volume of 100 gm. of chlorine at 15° and 410·4 mm. : $T = 273 + 15 = 288$, $p = 410{\cdot}4/760 = 0{\cdot}54$ atm.; $n = 100/71 = 1{\cdot}408$ mols ;

$$\therefore\ V = nRT/p = 1{\cdot}408 \times 0{\cdot}08208 \times 288/0{\cdot}54 = 61{\cdot}6 \text{ litres.}$$

Equations representing volume relations must always express the reactions between *molecules* of the gases · $N_2 + 3H_2 = 2NH_3$, not $N + 3H = NH_3$. The volumes of solids and liquids taking part may usually be neglected : Avogadro's hypothesis does not apply to them

Abnormal vapour densities.—Acetic acid has the empirical formula, *i e*, the simplest formula deduced from its percentage composition, CH_2O. Its vapour density at 250° and 760 mm pressure is 29 (H = 1), hence the molecular weight is 58 But $C_2H_4O_2 = 60$, hence under these conditions the vapour has this formula. At lower temperatures, at 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 The changes with temperature and pressure occur *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 $C_4H_8O_4$, *i e*, the substance is **associated.** By rise of temperature, or decrease of pressure, the associated molecules *gradually* break up into normal molecules : $(C_2H_4O_2)_2 \rightleftharpoons 2C_2H_4O_2$

A different behaviour is shown by another group of substances, of which ammonium chloride is typical The solid salt is produced by the direct union of ammonia, NH_3, with hydrogen chloride, HCl, and its simplest formula is NH_3,HCl, or $NH_4Cl = 53·2$ Bineau found the vapour density 12·4, giving a molecular weight of 24·8, half the least possible theoretical value, and corresponding with the formula $N_1H_2Cl_1$. 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 1857–58.

Dissociation by heat.—Mitscherlich in 1833 had observed that antimony pentachloride on volatilisation by heat breaks up partly into antimony trichloride and free chlorine · $SbCl_5 = SbCl_3 + Cl_2$. These 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 progressive 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 after cooling.

J. H. Gladstone (1849) found that the pale yellow solid phosphorus pentabromide partly 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, and 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, dissociates into ammonia and hydrogen chloride:

$$NH_4Cl \rightleftharpoons NH_3 + HCl,$$

which recombine on cooling. The density for complete decomposition is half the theoretical density, because the volume is doubled by decomposition. Pebal (1862) confirmed this assumption by separating the two gases, NH_3 and HCl, from the vapour by diffusion Ammonia is much lighter than hydrogen chloride and diffuses more rapidly.

Pebal used the apparatus shown in Fig. 63 The tube *D* contained a plug of asbestos, *c*, and above this was a piece of ammonium chloride, *d*. The tube was enclosed in a wide test-tube, contained in a jacket

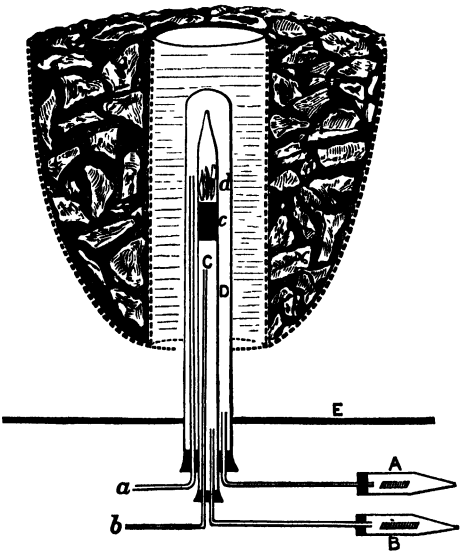


FIG 63.—Pebal's experiment on the dissociation of ammonium chloride

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 hydrogen chloride; the latter was swept out through the other tube, and turned the litmus red.

Deville objected that the vapour might have been decomposed by the asbestos plug. Than in 1864 replaced the latter by a plug of solid ammonium chloride (Fig 64) and obtained the same result The dissociation of ammonium chloride was proved.

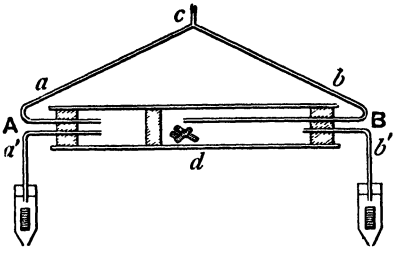


FIG 64.—Than's experiment on the dissociation of ammonium chloride

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 hydrogen chloride combine to produce the compound, and hence the compound must decompose into the two gases on volatilisation.

In dissociation, as in association, the change occurs progressively, 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 example, in the progressive darkening in colour of the vapour of phosphorus pentabromide. The dissociation of colourless hydrogen iodide gas on heating is seen from the violet colour of the iodine vapour produced: $2HI \rightleftharpoons H_2 + I_2$.

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.

Determination of dissociation from vapour density.—The **degree of dissociation**, γ, *i.e.*, the fraction of the total number of molecules dissociated, can be deduced from the vapour density, except in cases where there is no change of volume on dissociation, *e g*, $HI + HI \rightleftharpoons H_2 + I_2$.

In the dissociation of substances such as phosphorus pentachloride, when a change of volume occurs:

$$\underset{1 \text{ vol}}{PCl_5} \rightleftharpoons \underset{2 \text{ vols.}}{PCl_3 + Cl_2}$$

let each molecule of the initial substance give x molecules on dissociation. Then from N molecules of substance we obtain:

$N(1-\gamma)$ molecules of original substance,

$Nx\gamma$ molecules of the products of dissociation.

The number of molecules before dissociation is N; that after dissociation is $N(1-\gamma) + Nx\gamma = N[1+\gamma(x-1)]$, and 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 Δ be the normal vapour density, corresponding with the undissociated substance, and D the observed vapour density, then :

$$\Delta = D[1 + \gamma(x - 1)];$$

$$\therefore \gamma = \frac{\Delta - D}{D(x - 1)}$$

The vapour density corresponding with complete dissociation is $d = \Delta/x$ In the case of phosphorus pentachloride, $x = 2$, hence : $\gamma = (\Delta - D)/D$, and $d = \frac{1}{2}\Delta$, *i e*, on complete dissociation the vapour density has half the normal value.

At 200° and 1 atm pressure, the vapour density of phosphorus pentachloride is 70·03 (O = 16) The density corresponding with no dissociation is $\frac{1}{2}PCl_5 = 103{\cdot}35$. Thus, $\Delta = 103{\cdot}35$, $D = 70{\cdot}03$, and $\gamma = \frac{103{\cdot}35 - 70{\cdot}03}{70{\cdot}03} = 0{\cdot}476$. Out of every 1000 molecules of PCl_5, 476 are dissociated into $PCl_3 + Cl_2$. The vapour densities and dissociations at various temperatures at 1 atm press. are (Cahours, 1847) :

$t°$ -	182	190	200	230	250	274	288	300
D -	73 36	72 06	70 03	69 21	57 77	55·46	53 01	52·71
γ -	0 409	0 434	0 476	0 493	0 788	0 864	0 950	0·961

Types of chemical reactions.—The elements chlorine and hydrogen react to form the compound hydrogen chloride ; this is called **combination.** By suitable means (*e g* , electrolysis) it is possible to recover from the compound 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 atoms. With the advent of the molecular theory, the point of view was altered and the reactions were formulated as follows

(1) $H_2 + Cl_2 = 2HCl$, or $HH + ClCl = HCl + HCl$;

(2) $2HCl = H_2 + Cl_2$, or $HCl + HCl = HH + ClCl$.

They are now seen to be examples 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 $HH + II = HI + HI$ 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 $2HI = H_2 + I_2$

In the case of **isomeric change** (p 93) there are two possibilities: (1) the different substances of the same empirical formula have the *same molecular weight*; they are then sometimes called **metamers**; 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.**

Examples of metamerism are hyponitrous acid and nitramide, both having the formula $H_2N_2O_2$ In hyponitrous acid the atoms are arranged according to the formula $(HON)_2$, whilst in nitramide the arrangement is NH_2NO_2 An example of polymerisation is that of acetic acid (p. 123) Sometimes a polymer of twice the molecular weight of the simplest form is called a **dimeric form**, and so on Sulphur vapour contains the molecules S_8 and S_6, perhaps also S_4, as well as S_2. At very high temperatures it contains only S_2 and S.

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 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 at very low pressures; under ordinary conditions it is only approximate

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 occurs in a molecule of a compound.* In some cases the atom is identical with the molecule, but usually the molecule consists of two or more atoms

The **molecular weight** of a substance (H = 1) 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, since the hydrogen molecule contains two atoms, H_2 On the oxygen standard (O = 16), the standard is one-sixteenth the weight of an atom of oxygen, and the factor for converting relative density (H = 1) to molecular weight is 2·016, or 2 if the relative density is also referred to O = 16

The molecular weight (O = 16) in grams of any gas (**gm. mol.** or **mol**) occupies at S T.P. a volume of 22·415 litres (**gm. mol. vol.** or **molar volume**).

If n mols of a gas or vapour occupy V litres under a pressure of p atm. and at an absolute temperature $T = t° \text{ C} + 273$, then

$$pV = nRT,$$

where R is the **gas constant**; in the units stated, $R = 0.08208$ litre atmospheres

Many compounds on heating **dissociate**, *i.e.*, are partly decomposed, to an extent increasing with 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 broken up, may be calculated from the equation, $\gamma = (\Delta - D)/D(x - 1)$, where Δ = density of undissociated substance; D = observed density, both reduced to S T P, and x = number of molecules formed on dissociation from one molecule of the substance.

CHAPTER X

OXYGEN

Occurrence of oxygen.—The element oxygen 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. Oxygen occurs to the extent of 21 per cent by volume or 23 per cent by weight in the atmosphere, and takes part in processes of combustion; its biological functions in respiration make it important The gas 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. Its solubility in sea water is about 0·78 that in pure water.

Combined oxygen occurs in water, in vegetable and animal tissues, in nearly all rocks and in many minerals: it occurs to a larger extent (about 50 per cent.) in the earth's crust than any other element.

Oxygen was first isolated by Scheele in 1772, and was discovered independently by Priestley in 1774 (p. 38).

The Egyptian chemist Zosimos (250 A D) refers to a gaseous body evolved on heating a substance floating on the surface of heated mercury (possibly mercury oxide) According to Klaproth, the Chinese philosopher Mao Khoá (750 A.D) 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)

Preparation of oxygen.—Oxygen may be obtained by heating certain **metallic oxides**, viz., those of mercury, silver, gold, and the platinum metals. Mercuric oxide, heated in a hard glass tube, 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. 18). Oxide of silver, precipitated from silver nitrate solution by caustic potash (in absence of carbon dioxide), gives very pure oxygen when heated: $2Ag_2O = 4Ag + O_2$.

Oxides of other metals are stable at high temperatures, but some

higher oxides of metals, and hydrogen peroxide, on heating decompose into oxygen and lower oxides :

$$2H_2O_2 = 2H_2O + O_2.$$
$$2BaO_2 = 2BaO + O_2.$$
$$2PbO_2 = 2PbO + O_2.$$
$$3MnO_2 = Mn_3O_4 + O_2 \text{ (at a bright red heat).}$$

Manganese dioxide evolves oxygen more readily when heated with concentrated sulphuric acid :

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

Oxygen may be obtained from **water** by electrolysis (p 50), or by removing the hydrogen with chlorine ; the latter combines with hydrogen to form the stable hydrogen chloride, HCl, but does not unite directly with oxygen : $2H_2O + 2Cl_2 = 4HCl + O_2$.

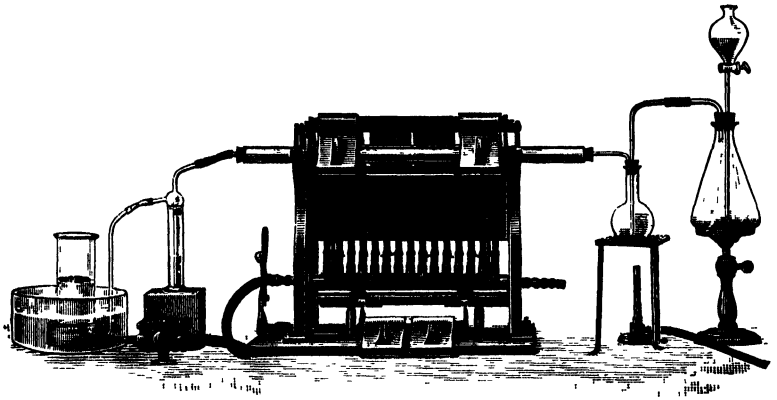


FIG 65 —Decomposition of steam, by chlorine

EXPT 1 —A stream of chlorine is passed through water boiling in a 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 65). The gas is passed through caustic soda solution in a wash-bottle to remove excess of chlorine, and hydrochloric acid, and the oxygen collected over water.

Some **salts rich in oxygen** : chlorates (*e.g.*, $KClO_3$), bromates, iodates, nitrates, dichromates (*e g.*, $K_2Cr_2O_7$), and permanganates (*e g.*, $KMnO_4$) evolve oxygen on heating.

In the production of oxygen by heating nitre, when potassium nitrite is left as a residue : $2KNO_3 = 2KNO_2 + O_2$, a fairly high temperature is required.

Potassium chlorate crystals are anhydrous; they melt at 357°, and on heating at 380° in a hard glass tube evolve oxygen: (1) $2KClO_3 = 2KCl + 3O_2$. As the reaction proceeds, the evolution of gas slackens, and the salt becomes pasty, finally almost solid, although decomposition is not complete. At this stage the residue contains potassium chloride and **potassium perchlorate**, $KClO_4$, produced by the reaction: (2) $4KClO_3 = 3KClO_4 + KCl$. If the temperature is raised the mass fuses again ($KClO_4$ melts at 610°), oxygen is evolved, and finally solid potassium chloride (m. pt. 800°) remains: (3) $KClO_4 = KCl + 2O_2$. Reactions (1) and (2) proceed simultaneously and *independently* from the commencement.

At high temperatures the gas contains a little chlorine owing to the reaction (4) $4KClO_3 = 2K_2O + 2Cl_2 + 5O_2$, which takes place to a slight extent A mixture of potassium and sodium chlorates liberates oxygen at a lower temperature than potassium chlorate alone

Potassium permanganate on heating at 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 cooled residue, a dark green solution of the manganate is formed

A solution, or paste, of **bleaching powder**, heated with a few drops of cobalt chloride solution, rapidly evolves oxygen (Mitscherlich, 1843), The bleaching powder, $CaOCl_2$, is decomposed by water into calcium chloride and calcium hypochlorite:

$$2CaOCl_2 = CaCl_2 + Ca(OCl)_2.$$

Cobaltous oxide is precipitated by the free lime always contained in the bleaching powder.

$$(a)\quad CoCl_2 + Ca(OH)_2 = CoO + CaCl_2 + H_2O,$$

but is at once converted by the oxidising action of the hypochlorite into a black peroxide CoO_2:

$$(b)\quad 2CoO + Ca(OCl)_2 = 2CoO_2 + CaCl_2.$$

This peroxide CoO_2 (or possibly Co_4O_7, or CoO_3) then acts as a catalyst (p. 133) in promoting the decomposition of the calcium hypochlorite.

EXPT. 2.—Add caustic soda solution to cobalt chloride solution: a blue precipitate, rapidly turning to a pink precipitate of hydrated CoO, is thrown down. Pour this into bleaching powder solution. The precipitate at once becomes oxidised to a black substance, CoO_2, and oxygen is freely evolved on warming

Chromium trioxide and **potassium dichromate** evolve oxygen when heated with concentrated sulphuric acid, the red colour of these compounds changing to olive-green :

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + 2CrO_3 + H_2O;$$
$$4CrO_3 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 6H_2O + 3O_2$$

Chromium trioxide decomposes when heated alone, although a little sublimes unchanged : $4CrO_3 = 2Cr_2O_3$ (green) $+ 3O_2$

Potassium dichromate (m.pt. 396°) when strongly heated evolves oxygen :

$$4K_2Cr_2O_7 = 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

Potassium permanganate explodes violently when warmed with concentrated sulphuric acid, but readily yields pure oxygen if **hydrogen peroxide** solution is mixed with a solution of the permanganate and 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. 3 —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 " 20 volumes " hydrogen peroxide in a flask. The oxygen evolved is collected over water

Oxygen is evolved when water is dropped on sodium peroxide or on a mixture of barium peroxide and potassium ferricyanide :

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$
$$BaO_2 + 2K_3Fe(CN)_6 = K_6Ba[Fe(CN)_6]_2 + O_2,$$

or when barium peroxide is treated with ferric chloride solution :

$$6BaO_2 + 4FeCl_3 + 6H_2O = 6BaCl_2 + 4Fe(OH)_3 + 3O_2$$

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. Only the chlorate is decomposed.

EXPT 4 —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.

A mixture of 5 gm. of manganese dioxide with 25 gm. of potassium chlorate (**oxygen mixture**) evolves oxygen freely when heated in a glass tube at a temperature below the melting point of the chlorate. The heating must be carefully regulated, as the decomposition of potassium chlorate, unlike that of mercuric oxide, *evolves* heat and under certain conditions may become explosive.

The manganese dioxide undergoes no permanent chemical change in the reaction: it may be recovered by dissolving out the potassium chloride from the residue with water.

EXPT 5.—Mix 25 gm. of potassium chlorate with 5 gm. 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. Fit the tube in a horizontal position with a good cork and a wide ($\frac{1}{4}$ in.) glass delivery tube to a Woulfe's bottle containing caustic soda solution, Fig. 66. The caustic soda removes any chlorine from the gas. 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*.

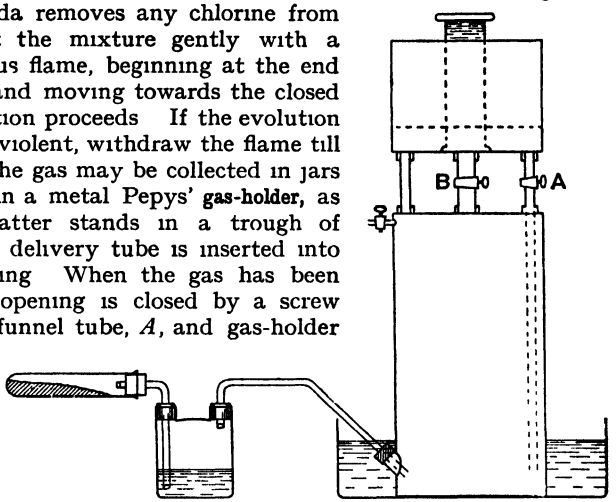


FIG. 66.—Preparation of oxygen from potassium chlorate and manganese dioxide

Warning.—Manganese dioxide adulterated with powdered coal 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 and cupric oxide, act similarly to manganese dioxide: they are also left chemically unchanged after the reaction. This action, discovered by Dobereiner in 1820, is an example of numerous cases in which a substance accelerates a chemical reaction without itself undergoing any permanent chemical change. Such substances were called **catalysts** by Berzelius (1835).

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. 43) :

$$S + O_2 = SO_2\,,\quad SO_2 + H_2O = H_2SO_3 \text{ (sulphurous acid).}$$
$$2S + 3O_2 = 2SO_3\,;\quad SO_3 + H_2O = H_2SO_4 \text{ (sulphuric acid)}$$
$$4P + 5O_2 = 2P_2O_5\,;\quad P_2O_5 + H_2O = 2HPO_3 \text{ (metaphosphoric acid)}$$
$$C + O_2 = CO_2\,;\quad CO_2 + H_2O \rightleftharpoons H_2CO_3 \text{ (carbonic acid)}$$

EXPT. 6.—Magnesium ribbon, ignited in air and inserted into oxygen, burns with a blinding white light, forming white solid magnesium oxide, MgO, which is weakly basic and turns moist red litmus paper blue. Sodium and potassium, heated in iron deflagrating spoons until they begin to burn, and then lowered into *dry* jars of oxygen, burn with bright yellow and lilac flames, respectively, forming orange-yellow solid peroxides which dissolve in water with evolution of oxygen and formation of strongly alkaline hydroxides

$$2Na + O_2 = Na_2O_2\,;\quad 2Na_2O_2 + 2H_2O = 4NaOH + O_2\,;$$
$$2K + 2O_2 = K_2O_4\,;\quad 2K_2O_4 + 2H_2O = 4KOH + 3O_2$$

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, unless it contains a layer of sand

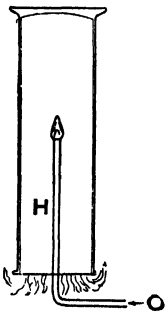


FIG. 67 — Oxygen burning in hydrogen

A jet of hydrogen burns in a dry jar of 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 67). The terms **combustible**, and **supporter of combustion**, are, therefore, purely relative

EXPT 7.—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 (Fig. 68). The oxygen from the chlorate, if the latter is sufficiently heated, takes fire, and burns violently 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 8.—By means of a brush trace letters on a piece of paper with a solution of phosphorus in carbon disulphide. When the solvent evaporates, the finely divided phosphorus ignites, leaving charred letters on the paper.

EXPT 9.—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 **pyrophoric lead** shaken out, the metal glows brightly, forming yellow fumes of lead oxide, PbO.

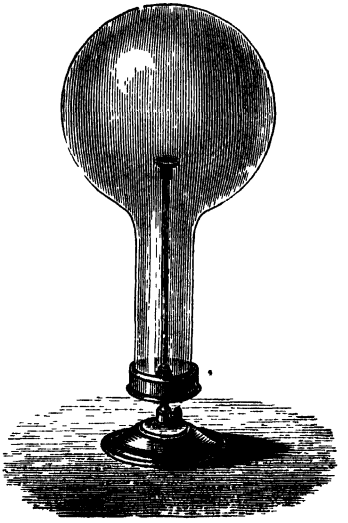


FIG. 68.—Apparatus for combustion.

Many substances, such as phosphorus, oxidise slowly when exposed to air, 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 process of slow 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 to form a non-explosive mixture, and passing over platinised asbestos at a dull red heat, or gently heated palladium, 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 oxide 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.**

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, 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 therefore serve to bring about the decomposition, or other chemical change, of large quantities of materials.

The first reasonable **theory of catalytic action** was due to Clement and Desormes (1806), who assumed that the reacting substances and the catalyst form an unstable **intermediate compound,** which then breaks up, reproducing the catalyst in its original chemical composition, and liberating the products 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, in the present case, J. Mercer (1842) assumed that 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. 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:

$$KClO_3 + 2MnO_2 = KCl + Mn_2O_7 = KCl + 2MnO_2 + 3O.$$

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:

$$K_2O,Cl_2O_5 + WO_3 = K_2O,WO_3 + Cl_2O_5 = K_2O,WO_3 + Cl_2 + 5O$$

EXPT. 10.—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 (1) oxygen is evolved, (11) 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 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. 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. 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.

Technical preparation of oxygen.—Various methods have been applied for the production of oxygen on the large scale, but at the present day two types of process are almost exclusively in use, viz., the **electrolysis of water** (with simultaneous production of hydrogen), and the **fractional distillation of liquid air.**

One type of electrolytic apparatus consists of an iron tank containing a solution of caustic soda, in which are immersed a number of iron bell-jars, each provided with an insulated iron electrode dipping below the mouth of the bell. The electrodes are connected to the positive and negative poles of a dynamo, and the oxygen and hydrogen gases liberated pass inside the bell-jars and are led off through pipes.

The electrolyte is kept at about 60° and large currents (up to 1000 amperes) may be used

A number of chemical methods were formerly used for the production of oxygen, the most important being the **Brin process.**

Boussingault in 1852 showed that baryta, BaO (which is a substance similar to quicklime, CaO), heated in a porcelain tube to *dull redness*, can absorb oxygen from air passed over it, 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 *reversible*, and proceeds in one direction or the other according to the temperature: $2BaO_2 \rightleftharpoons 2BaO + O_2$ By using purified air, and iron retorts heated by gas at about 700°, the brothers Brin in 1879 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. This **Brin process** was the principal technical method until 1902; it has now given way to the liquid air process (p. 143)

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 80). By working under pressure, and repeating the process four or five times, Mallet obtained a gas containing over 75 per cent. of oxygen

When 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)

$$\frac{\text{Speed of diffusion of nitrogen}}{\text{Speed of diffusion of oxygen}} = \frac{\sqrt{16}}{\sqrt{14}} = \frac{1\ 07}{1\ 00}$$

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 the method failed, owing to the small difference of densities.

Liquefaction of gases.—Ammonia gas was liquefied by compression by Van Marum, and in 1799 by cooling, by Guyton de Morveau. Sulphur dioxide was liquefied by cooling by Monge and Clouet; in 1806 chlorine was reduced to the liquid state by Northmore. In 1823 liquid chlorine was again obtained by Faraday, by warming chlorine

hydrate, at the suggestion of Davy, 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; the pressures in atm. required to liquefy the gases at 0° are:

Sulphur dioxide -	1·53	Ammonia - -	4·26
Chlorine - - -	3·66	Carbon dioxide -	34·55

The application of pressures up to 2000 atm. was tried without result by Natterer (1844) in the case of the gases nitrogen, oxygen, and hydrogen.

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 temperature of oxygen is −118·75° and the critical pressure 50·2 atm.

The critical temperatures of the so-called **permanent gases** lie below the lowest temperatures attained by older experimenters. As soon as it was clear that strong cooling was necessary and that high pressures alone could never succeed in the case of these gases, the problem was solved, independently, by Pictet and Cailletet in 1877.

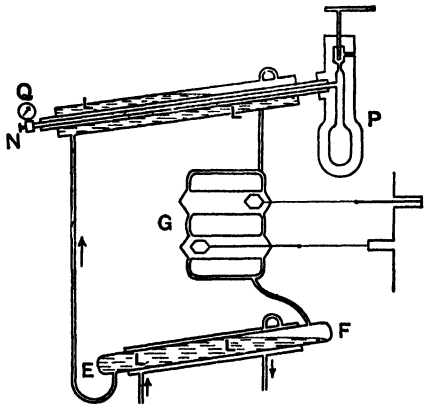


FIG. 69.—Liquefaction of oxygen by Pictet

Pictet used the apparatus shown in Fig 69. Oxygen generated in the retort *P* by heating potassium chlorate, was compressed by its formation in a copper tube, cooled in liquid carbon dioxide *L* boiling under reduced pressure, and fitted with a pressure gauge *Q* and release valve *N*. The carbon dioxide was reliquefied by a pump *G* in a second copper tube, *EF*, surrounded by liquid sulphur dioxide boiling under reduced pressure, and circulated by a second pump. Pictet reduced the temperature

to −140°, and the pressure rose to several hundred atmospheres. On opening the release-valve *N*, a jet of liquid oxygen issued from it, at once boiling away.

Cailletet compressed the gas by a powerful pump forcing water into a strong steel vessel, *B*, Fig. 70, in which the gas was contained in a tube, *T*, sealed below by mercury Water forced into *B* drove the mercury into *T*, and strongly compressed the gas The pressure was then suddenly released by opening a valve which allowed the water to escape, and the gas expanded suddenly (**adiabatic expansion**) 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

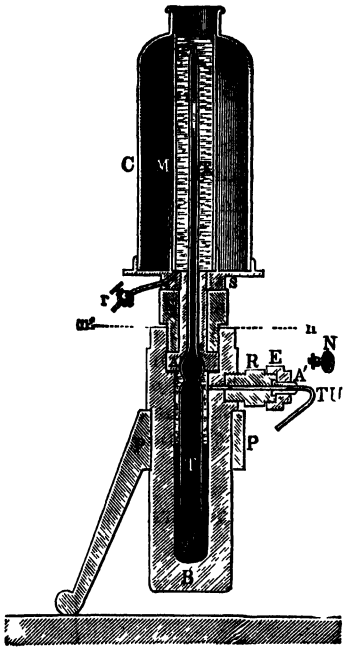


FIG. 70 —Liquefaction of gases by Cailletet

Liquid air.—The liquefaction of air in bulk was effected in 1895, independently, by Hampson in England and by Linde in Germany, who made use of a new principle, viz , the **Joule Kelvin effect,** investigated by Joule and William Thomson (later Lord Kelvin) from 1852 to 1862 When a compressed gas escaped into the free air through a plug of silk in a boxwood tube, a slight cooling effect occurred with most gases (air, oxygen, nitrogen, carbon dioxide), but with hydrogen alone there was a slight heating effect.

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_1 (Fig. 71), 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. 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, $p_1v_1 = p_2v_2$ ($v_2 = 2v_1$; $p_1 = 2p_2$), and no *external* work would be done ; 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

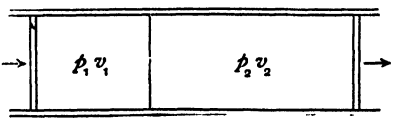


FIG. 71 —Diagram illustrating free expansion of gases

the gas will have separated, and since a slight attraction exists between them, *internal* work will have been spent in separating the molecules. The energy required for this *internal* work is taken from the heat of the gas, and a slight cooling effect 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 much more is absorbed to supply the internal work.

In the case of air the cooling effect in degrees C. is given by

$$\frac{\text{difference of pressures in atm.}}{4} \times \left(\frac{273}{T_1}\right)^2,$$

where T_1 is the absolute temperature of the air before expansion.

If air at 0° C., and under a pressure of 100 atm , is expanded through a valve to atmospheric pressure, the fall of temperature will be

$$\frac{99}{4} \times \left(\frac{273}{273}\right)^2 = 24\ 7°.$$

If this cool air, at $-24{\cdot}7°$, sweeps over the surface of a copper pipe, bringing compressed air to the valve, by placing the latter inside the pipe taking away the cold expanded air (Fig 72), the expanded air abstracts heat from the air coming to the valve, becoming itself warmed nearly to the atmospheric temperature The cooled compressed air at $-24{\cdot}7°$ will, after expansion, become 30·3° colder, as the above formula shows, and this cold air at $-55°$ sweeps over the inner tube, reducing still further the temperature of the compressed air coming down The cooling effect *accumulates*, and the air issuing from the nozzle finally becomes so cold that it liquefies

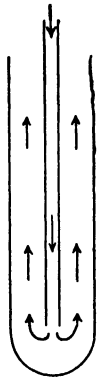


FIG 72 — Cooling of gases by free expansion

This apparatus, called a **heat-interchanger**, was applied by Hampson and by Linde to the liquefaction of air on a large scale. A diagrammatic representation of an air liquefaction apparatus, which is self-explanatory, is given in Fig. 73.

Liquid air is kept in double-walled **Dewar ("thermos") flasks** (Fig. 74), the inner surfaces of which, silvered to reflect heat, have a high vacuum between them to cut down heat transmission to a minimum.

Liquid air is usually slightly turbid, because it contains particles of ice and solid carbon dioxide. If filtered through a large filter paper it forms a clear liquid, with a pale blue colour, due to liquid oxygen. 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 elastic, and rubber hard and brittle. Mercury is at once frozen to a malleable solid. Raw meat, fruits, flowers, etc., become

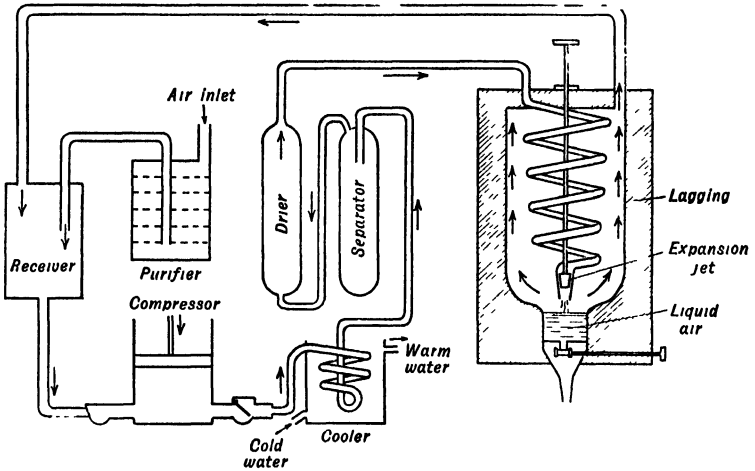


FIG. 73.—Production of liquid air

The air is drawn by a pump through a purifier, and is compressed. The heat produced by compression is taken out by a cooler, and the air then passes through apparatus in which moisture is removed The compressed air expands through a jet, and becomes cooled. The cold air sweeps over the pipe bringing the compressed air to the jet and cools it before expansion. The air finally becomes so cold that it liquefies.

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 "steam," *i.e.*, atmospheric moisture condensed to particles of ice by the cold of the escaping evaporated air, are emitted from the spout. The phosphorescence of calcium sulphide is at once quenched at the temperature of liquid air, but appears again on warming. Sulphur and mercuric iodide become much paler in colour on cooling in the liquid.

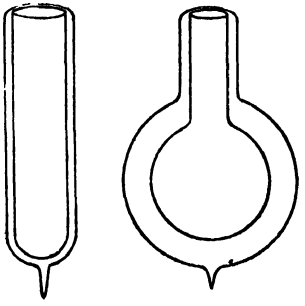


FIG 74 —Vacuum vessels

On standing, liquid air becomes bluer in colour; the more volatile, colourless nitrogen (b. pt. $-195{\cdot}7°$) escapes, and pale-blue **liquid oxygen** (b. pt. $-182{\cdot}9°$) is left. A cigarette soaked in liquid oxygen burns rapidly when lighted; a stick of carbon heated to redness burns brightly under

the surface of liquid oxygen in a beaker, as does a piece of iron wire tipped with burning wood; and with a little care a hydrogen flame can be plunged into the liquid and continues to burn, producing an appreciable amount of ozone, recognisable by the smell.

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, when the nitrogen would pass off and liquid oxygen might be left This would, however, lead to serious loss of oxygen, as is seen from the table below, giving the results of Linde's experiments:

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 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 air or oxygen passing down in the opposite direction.

Claude in 1906 introduced two new principles: (1) he liquefied the air in stages, obtaining two liquids, one rich in oxygen and the other in nitrogen; (2) the expanding gas was allowed to do work in an engine, and the heat equivalent of this work was taken from it. (This had been previously suggested by Rayleigh.) A tall 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. 75 Compressed air at about 20–35 atm, cooled by an interchanger as in the Linde process, enters *A*, already partly liquefied, into a vessel containing two sets 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.

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 oxygen gas from *S* goes off by the pipe *G* to the heat-interchanger where its cold is utilised, after which it is pumped at 120 atm pressure into steel cylinders for use. The compressed air 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 being richer in **nitrogen**. This 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 Gas rich in nitrogen escapes at the top of the column and its cold is utilised in the heat interchangers The liquid condensed in the inner pipes is scrubbed by air passing on.

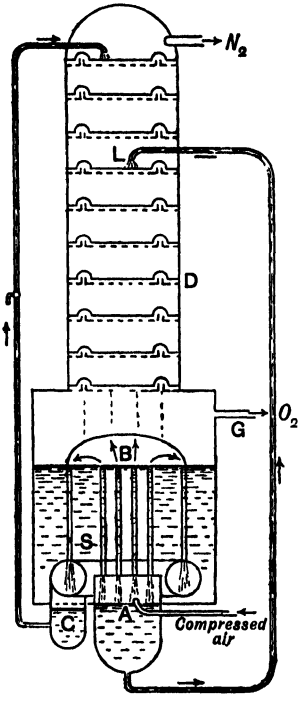


FIG 75 —Claude's oxygen apparatus

Liquid air as obtained from the liquefier is richer in oxygen than gaseous air. Usually it contains from 50 to 60 per cent. by weight of oxygen as compared with 23 in gaseous air.

Liquid air or oxygen 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 exhausted. A high vacuum is produced 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 at high altitudes, 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 mouthpiece. The controlling mechanism consists of a siphon dropping liquid oxygen at a controlled rate into an evaporation chamber. This control is necessary, since great fluctations in the rate of evaporation are caused by movements from higher to lower altitudes where the atmospheric pressure is higher

Solid oxygen (blue) is obtained by cooling the liquid in a tube immersed

in liquid hydrogen It cannot be obtained by the rapid evaporation of the liquid, as is the case with solid nitrogen Liquid oxygen is strongly magnetic; the gas is weakly magnetic A second, denser form of the solid probably exists at temperatures much below the melting-point, which is $-219°$ at 12 mm pressure.

About 85 per cent. of the commercial oxygen is used, in about equal proportions, for cutting and welding metals by the oxy-acetylene or oxy-coal gas blowpipe (p. 153). The rest is used in medicine for treating cases of pneumonia, gas-poisoning, etc., for oxidising linseed oil, for maturing spirits, for the conversion of acetaldehyde into acetic acid, absorbed as liquid in charcoal as an explosive, and in the synthesis of nitric acid.

CHAPTER XI

HYDROGEN

Occurrence of hydrogen.—Although an inflammable gas (*gas pingue*) is mentioned by Van Helmont, and the preparation, collection and combustion of hydrogen are described by Boyle, it was first adequately investigated by Cavendish in 1766.

In the free state hydrogen occurs in traces in volcanic gases; those evolved in the eruption of Mt Pelée in 1902 contained 22·3 per cent. hydrogen. It also occurs in small cavities in rock-salt, and various minerals and rocks, such as apatite, serpentine, gneiss, blue-clay, Peterhead granite, basalt, and beryl, evolve hydrogen on heating. It occurs in the atmosphere, but only to the extent of about 0·01 per cent., and is found in the earlier fractions of the gases from liquid air. Meteorites composed chiefly of iron with nickel and cobalt contain hydrogen. 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 500,000 miles into space. Hydrogen is produced in certain types of fermentation of carbohydrates brought about by specific bacteria

Hydrogen occurs chiefly in combination with other elements, especially with oxygen in the form of water, H_2O, and with carbon as **hydrocarbons**; the gas issuing from fissures in coal often consists of nearly pure **methane**, CH_4; more complicated hydrocarbons make up **petroleum**. All animal and vegetable matter and coal, contain hydrogen, and gaseous hydrogen compounds found in nature are the sulphide (H_2S), phosphide (PH_3), ammonia (NH_3), and, in volcanic gases, the chloride (HCl), bromide (HBr), and iodide (HI). All acids and alkalies contain hydrogen.

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 several ways.

By electrolysis (p. 50) both hydrogen and oxygen are produced, theoretically in the volume 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," to persulphuric acid, $H_2S_2O_8$, at the anode. Some hydrogen peroxide, H_2O_2, is formed at the cathode The presence of these oxidising agents in the liquid may be shown by adding a solution of potassium iodide and starch, when a blue colour, due to liberation of iodine, appears. The oxygen evolved may also contain a little ozone, O_3. If the liquid is electrolysed hot or phosphoric used instead of sulphuric acid, no ozone is formed and the volumes are nearly in the ratio 2 : 1.

Hydrogen is set free by the action of certain metals on water. Sodium and potassium react violently with cold water :

$$2Na + 2H_2O = 2NaOH + H_2.$$

EXPT 1 —A *small* piece of potassium thrown on water floats, and the hydrogen takes fire and burns with a lilac 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, if it contains more than 1 per cent. of sodium, is solid at the ordinary temperature.

EXPT. 2 —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.

Calcium decomposes cold water slowly :

$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

Boiling water is decomposed readily by ordinary magnesium powder, by aluminium powder, and by copper-zinc couple, prepared by the action of copper sulphate solution on zinc :

$$Zn + 2H_2O = Zn(OH)_2 + H_2.$$

EXPT. 3.—Pour a 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. Hydrogen is evolved

Steam is decomposed by sodium, and by heated magnesium, zinc, iron, cobalt, lead, tin, and nickel, but not by silver or copper.

EXPT. 4.—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 may be burnt at the mouth of the flask. $Mg + H_2O = MgO + H_2$.

In the decomposition of steam by red-hot iron (p. 48), black oxide of iron, or **ferroso-ferric oxide**, Fe_3O_4, is formed, but the decomposition of the steam is incomplete. 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 heated 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 technical preparation of hydrogen. In the **Lane process** reduced iron, from spathic iron ore, is heated at 600°–850° in vertical iron retorts, and steam blown through. The iron oxide formed is reduced again with water-gas, a mixture of hydrogen and carbon monoxide, formed by passing steam over red-hot coke: $C + H_2O = CO + H_2$. The steaming and reduction processes alternate. The gas contains 98 per cent. of hydrogen and a little carbon monoxide. In the **Bosch process** water gas mixed with steam is passed over a heated catalyst consisting of ferric oxide with "promoters," such as chromium oxide (Cr_2O_3), which increase the activity of the catalyst. The carbon monoxide is decomposed by steam: $CO + H_2O \rightleftharpoons CO_2 + H_2$. The carbon dioxide is removed by washing with water at 25 atm. pressure, and the remaining trace of carbon monoxide by washing the gas, under 200 atm. pressure, with ammoniacal cuprous formate solution and with 25 per cent. caustic soda solution at 260°, in steel towers. $CO + NaOH = H.COONa$ (sodium formate).

Special processes for the production of smaller quantities 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 :

$$Si + 2NaOH + H_2O = Na_2SiO_3 \text{ (sodium silicate)} + 2H_2.$$

Hydrogen is also produced in the electrolysis of caustic soda solution with iron or nickel electrodes, and as a by-product in alkali manufacture

Hydrogen from acids.—Hydrogen is evolved by the action of zinc, magnesium and iron on dilute hydrochloric and sulphuric acids and by the action of concentrated hydrochloric acid on aluminium and tin. Nitric acid does not give hydrogen unless cold 2 per cent acid and magnesium are 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 on the **strength of the acid**, a property which must not be confused with the concentration

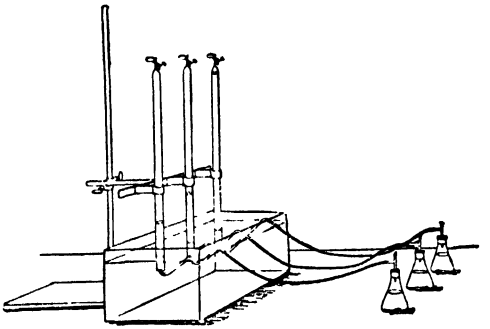


FIG 76.—Experiment to compare rates of evolution of hydrogen by zinc from different acids

EXPT 5. — Arrange three flasks with delivery tubes under graduated tubes in a pneumatic trough (Fig 76) In each place 5 gm. of zinc, and pour in 50 c c of solutions of hydrochloric (36 5 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 acids :

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
$$Zn + 2HCl = ZnCl_2 + H_2.$$

EXPT. 6.—A bottle is one-third filled with granulated zinc and fitted with a tap-funnel and delivery tube (Fig 77). Diluted hydrochloric acid (1 vol. of concentrated acid to 4 volumes of water), or dilute sulphuric acid (1 vol. of concentrated acid carefully poured into 5 vols. of

water, with stirring) is dropped in If very pure zinc is used, the reaction may be slow, but may be accelerated by adding a few drops of copper sulphate solution The gas is collected over water in jars, care being taken to allow all the air to be displaced from the apparatus a little gas collected in a test-tube should *burn* quietly, and not explode, as when air is present.

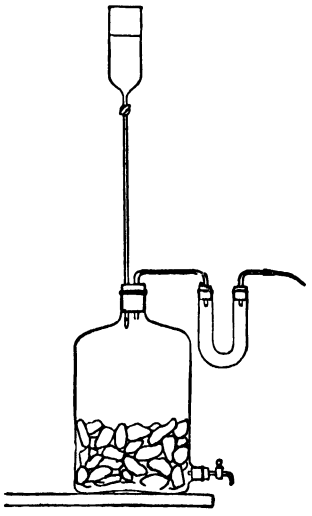


FIG 77.—Preparation of hydrogen

It the solution of zinc in sulphuric acid is filtered from black particles of lead or copper which were contained in the metal, slightly evaporated and set aside, colourless prismatic crystals of **zinc sulphate** (" white vitriol "), $ZnSO_4,7H_2O$, separate

Iron turnings may be used instead of zinc: $Fe+H_2SO_4=FeSO_4+H_2$, but 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 "), $FeSO_4,7H_2O$.

Purer gas may be obtained from dilute sulphuric or hydrochloric acid and 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. 78) may be used, the metal being placed in the central globe and acid poured in the top funnel until the lower bulb is full, and the metal covered with acid When the tap 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.

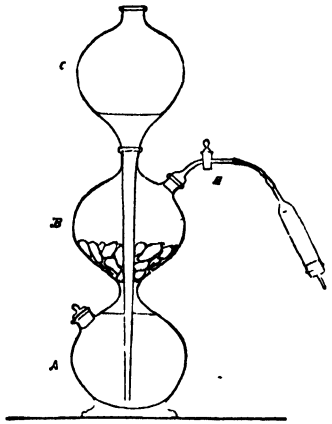


FIG 78.—Kipp's apparatus

The gas from zinc and sulphuric acid may contain some hydrogen sulphide, especially if the acid is hot, or the zinc

not quite pure. 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 hydrogen sulphide, phosphide and arsenide, and oxides of nitrogen, sulphur dioxide, and volatile hydrocarbons, are removed Unless hot copper is used, a little oxygen remains, but may be removed by a solution of chromous chloride or by passing over red-hot copper On a large scale, bleaching powder or a solution of bromine is used to remove arsenic compounds from the gas

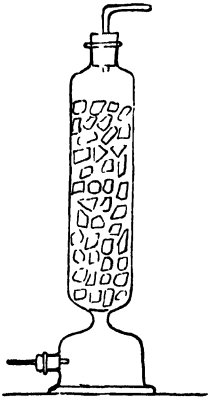


FIG. 79 —Drying tower

Hydrogen is *dried* by passing over granular calcium chloride, or broken sticks of caustic potash, in a tower (Fig 79) , final drying may be effected by phosphorus pentoxide dusted over plugs of glass-wool in a U-tube (Fig. 80). Sulphuric acid should *not* be used, as sulphur dioxide is formed $H_2SO_4 + H_2 = SO_2 + 2H_2O$, unless the acid is cooled in a freezing mixture.

Hydrogen from alkalies.—A solution of caustic soda or potash readily dissolves zinc or aluminium on warming, with evolution of hydrogen and formation of a soluble zincate or aluminate .

$$Zn + 2KOH = K_2ZnO_2 + H_2.$$
$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2.$$

Hydrogen prepared in this way is pure, and has no smell.

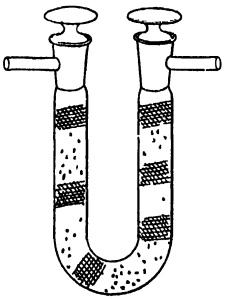


FIG. 80.—Phosphorus pentoxide drying tube.

EXPT. 7 —Heat 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.

Aluminium turnings may also be dissolved in *dilute* causitc soda solution by warming.

Pure hydrogen is evolved from the negative electrode by the electrolysis of a warm solution of recrystallised barium hydroxide, in a hard glass U-tube, with nickel electrodes (Fig. 81). This is sealed to U-tubes containing pieces of caustic potash, followed by tubes of pure phosphorus pentoxide, to dry the gas.

The hydrogen is first passed over heated platinum gauze, when oxygen from air-leaks and diffusion is 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 exhausted 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, when pure hydrogen is evolved

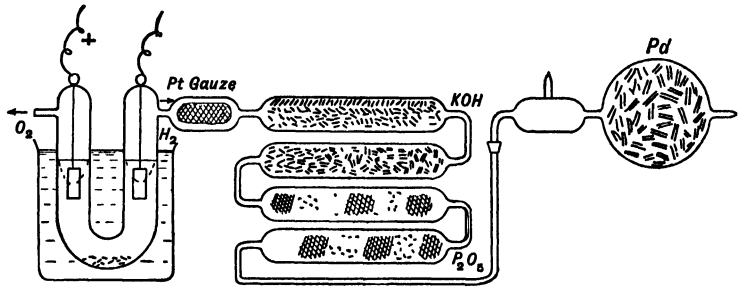


FIG 81 —Preparation of pure hydrogen by the electrolysis of barium hydroxide solution and absorption in metallic palladium

Nearly pure hydrogen may be prepared by electrolysing dilute sulphuric acid with an anode composed of a pool of zinc amalgam, which absorbs the nascent oxygen liberated at the anode :

$$Zn + O = ZnO \; ; \quad ZnO + H_2SO_4 = ZnSO_4 + H_2O.$$

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 hydrogen arsenide, is poisonous.)

Hydrogen is the lightest gas known, its normal density being 0·08987 gm. per litre. The solubility in water is not greatly affected by temperature : 0°, 0·0215 ; 10°, 0·0198 , 15°, 0·0190 ; 20°, 0·0184.

The **spectrum** of hydrogen, obtained by an electrical discharge in a Geissler tube, contains four bright lines, frequently used in calibrating spectroscopes or refractometers a red line H_α (Fraunhofer's C), 6562 A.U. ; a blue line, H_γ, 4340 A.U. ; a greenish-blue line, H_β (Fraunhofer's F), 4861 A.U. , and an indigo line, H_δ, 4102 A.U. (1 Ångström unit = A.U. = 10^{-10} metre = 10^{-8} cm. is the unit of wavelength).

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 : $c_p = 3{\cdot}4$ 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. At high temperatures a dissociation into atoms occurs: $H_2 \rightleftharpoons 2H$, the reaction absorbing a large amount of heat (about 100 k. cal. per mol.).

Chemical properties of hydrogen.—Hydrogen is a combustible gas, burning in air or oxygen to form water:

$$2H_2 + O_2 = 2H_2O.$$

Hydrogen and oxygen combine slowly at 180°, or in bright sunlight at the ordinary temperature Explosion occurs with moist gases at 550°–700°, 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 526° on adiabatic compression, some combination occurring before the explosion itself (pre-flame period) · the mixture $3H_2 + O_2$ ignites at 544°, and $H_2 + 4O_2$ at 478°, respectively (Dixon and Crofts, 1914) Thomas Thomson in 1817 gave 538° as the ignition temperature of hydrogen in air

Hydrogen also readily combines with fluorine and chlorine, less readily with bromine, iodine, sulphur, phosphorus, nitrogen, and carbon. With a few metals, such as lithium, sodium, and calcium, it forms **hydrides**, such as NaH. In these hydrides, which when pure are white salt-like compounds (KH explodes in air), readily decomposed by water:

$$NaH + H_2O = NaOH + H_2,$$

the hydrogen behaves to some extent like a halogen or electronegative element On the electrolysis of fused lithium hydride, the hydrogen is liberated at the *positive* electrode, not the negative as is the case when water is electrolysed (Moers, 1920). Hydrogen is also evolved at the anode in the electrolysis of a solution of calcium hydride, CaH_2, in fused potassium and lithium chlorides (Bardwell, 1924).

By reason of its tendency to unite with oxygen, hydrogen acts as a reducing agent. Hydrogen, when passed over many heated metallic oxides (copper, iron, lead), reduces them to the metallic condition, and water is produced: $CuO + H_2 = Cu + H_2O$ (*cf.* Expt. 9, p. 53) Reduction is in this case the withdrawal of oxygen. Some oxides, *e.g.*, of zinc and aluminium, are not reduced by hydrogen.

The oxy-hydrogen and oxy-acetylene blowpipes.—When oxygen and hydrogen are supplied separately to a blowpipe jet consisting (Fig 82) of two concentric metal 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, an intensely white light is emitted by the incandescent infusible lime, formerly used as **limelight.**

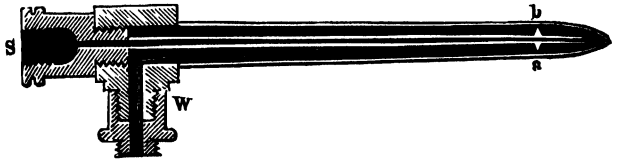


FIG. 82.—Oxy-hydrogen blowpipe

In the **oxy-acetylene blowpipe** acetylene gas takes the place of hydrogen or coal gas, and a hotter flame (3100°-3315°) is obtained. The steam formed 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 suitable for welding metals. In cutting iron or steel a third inner tube is used 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. The oxygen jet is narrow, and a very clean cut is produced. Plates of steel 12 in. thick can be rapidly cut through in this way. Coal gas may also be used.

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 may be "kapok," seed-hairs in the pods of a tree (*Eriodendron anfractuosum*) growing in India and Java.

Atomic hydrogen.—Langmuir (1912) has shown that hydrogen in contact with a tungsten wire heated by an electric current at low pressure, is dissociated into atoms: $H_2 \rightleftharpoons 2H$. This splitting of the hydrogen molecule is attended by the absorption of a large amount of energy, about 100 k. cal. per gram-molecule. The atomic hydrogen so formed is chemically very active. Langmuir also showed that atomic hydrogen is formed when an electric arc between tungsten electrodes is allowed to burn in hydrogen at atmospheric pressure (Fig. 83). The atomic hydrogen was blown out of the arc by a jet of molecular hydrogen directed across the arc, and formed an intensely hot flame, which is capable of melting tungsten (m. pt. 3400°). This flame obtains its heat not from combustion but from the recombination of hydrogen atoms to H_2. It is suitable for melting and welding many metals. Iron can be melted without contamination with carbon, oxygen, or nitrogen. Because of the powerful reducing action of the

atomic hydrogen, alloys can be melted without fluxes and without surface oxidation. A feature of the flame is the great rapidity with which heat can be delivered to a surface, which is very important in welding operations.

Nascent hydrogen.—Hydrogen being set free in a chemical reaction is often more reactive than hydrogen gas.

EXPT. 8.—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. 209):

$$FeCl_3 + H = FeCl_2 + HCl.$$

No such change is produced by bubbling gaseous hydrogen through the solution.

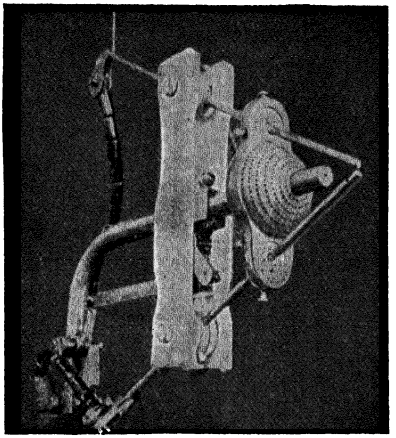


FIG. 83.—The atomic hydrogen blowpipe.

Hydrogen gas issues from the central nozzle on the right and is dissociated in an electric arc between two tungsten rods nearly meeting in a V.

Zinc and dilute sulphuric acid also reduce potassium chlorate to potassium chloride, as may be found by the addition of silver nitrate.

It is usually supposed that the activity of such hydrogen, sometimes called **nascent** (new-born), *i.e.*, in the act of liberation from its compounds, is due to the hydrogen being in the *atomic state*. Another theory is that the hydrogen is given off under a *great pressure*; 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 also of importance, because potassium chlorate is not reduced by sodium amalgam, which reduces nitrites to hyponitrites. Zinc reduces nitrites to ammonia in presence of alkali. 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 are used for reduction purposes. Hydrogen for reducing purposes may be liberated in alkaline solution by zinc or aluminium, and in neutral (aqueous) solution by copper-zinc couple or amalgamated aluminium. Gaseous hydrogen in presence of platinum or palladium black, or especially colloidal palladium, is a good reducing agent for solutions. At higher temperatures, hydrogen gas in presence of finely divided nickel is used to produce solid fats from liquid

oils, the oil taking up hydrogen. Hydrogen liberated by electrolysis at a cathode, especially of amalgamated lead, is a reducing agent.

The atomic character of nascent hydrogen is made probable by the following experiment. A stream of oxygen is allowed to bubble through a liquid around a cathode at which hydrogen is being liberated. Hydrogen peroxide is formed. Langmuir found that atomic hydrogen unites directly with oxygen to form hydrogen peroxide.

$$H + O_2 + H = HO \cdot OH.$$

Uses of hydrogen.—Hydrogen finds numerous uses in modern industry. In recent years its importance has greatly increased, owing to its use in the hardening of oils. An air-hydrogen blowpipe is used for the autogenous welding of lead sheets in the making of vitriol chambers (p 513); pure lead is used as a solder, being melted over the junction by the flame (" lead burning "). The oxy-hydrogen (or oxy-coal gas) 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 $N_2 + 3H_2 \rightleftharpoons 2NH_3$. Hydrogen is used in filling balloons and the gas containers of 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 $1·29 - 0·09 = 1·2$ km. The danger of fire in such cases is great, and in America hydrogen is replaced by helium. The hydrogen used in military balloons is usually transported in cylinders

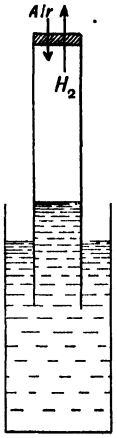


FIG 84.—Graham's diffusion apparatus

Diffusion of gases.—Hydrogen contained in an open *inverted* jar rapidly diffuses out, and air enters, this movement takes place in opposition to gravity. Dobereiner 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 dry plug of plaster of Paris. This tube is filled with water, the air being removed by a siphon so as to avoid wetting the plug, and the water displaced by hydrogen (Fig. 84). The water rises in the tube, and the latter may be sunk in a jar so as to keep the level constant.

After a 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 the volumes diffusing in equal times :

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 in the inverse ratio of the square-roots of the densities

$$\therefore \frac{\text{vol of hydrogen}}{\text{vol of air}} = \frac{\sqrt{1\ 293}}{\sqrt{0\ 09}}$$

$$\therefore \text{vol of air} = 100 \times \frac{\sqrt{0\ 09}}{\sqrt{1{\cdot}293}} = 26\ 4 \text{ c c.}$$

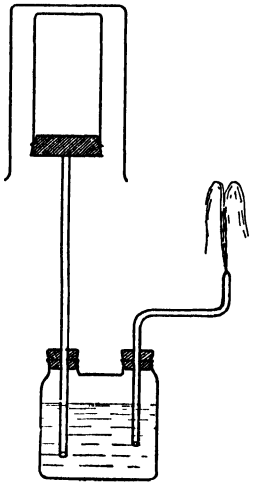


FIG. 85.—Experiment on diffusion.

EXPT 9 —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 in Fig 85 Dipping into the coloured water is a glass tube drawn out to a jet above A large beaker of hydrogen is inverted over the 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 removed, hydrogen inside the pot diffuses out more rapidly than air enters, so that the pressure is reduced and the water rises in the vertical tube

Liquid and solid hydrogen.—The first successful 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 colourless liquid hydrogen, readily boiling off Olszewski in 1895 found that the critical temperature of hydrogen is about $-234°$ (the accurate value is $-239·9°$; the critical pressure is 12·8 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.

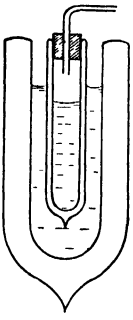


FIG 86.—Preparation of solid hydrogen

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 $-252·78°$. By rapidly evaporating the liquid under reduced pressure in a tube immersed in liquid hydrogen in a double Dewar vessel (Fig 86), 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 and neon are frozen to solids which at the extreme cold show practically no vapour pressure.

If a Geissler tube containing air 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 87).

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

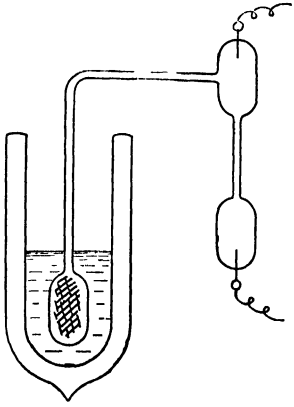


FIG. 87.—Experiment to show the very low temperature of liquid hydrogen

Liquid hydrogen may be prepared in the modification of Travers' apparatus devised by Nernst (Fig. 88). Compressed hydrogen enters through the copper coil, *A*, and passes through an extension, *A'*, of the coil immersed in liquid air in a large Dewar vessel. The cooled gas then passes 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* 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 The liquid air boiling in the outer Dewar 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

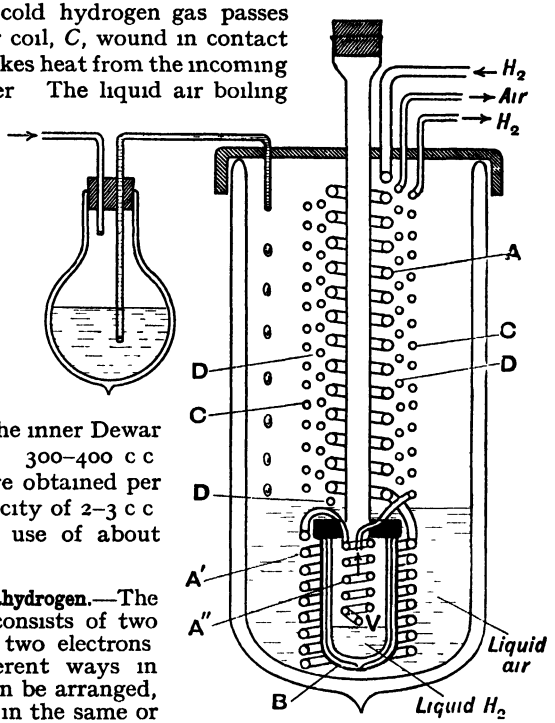


FIG 88.—Preparation of liquid hydrogen

Ortho- and parahydrogen.—The hydrogen molecule consists of two protons (p. 6) and two electrons There are two different ways in which the protons can be arranged, viz , with their spins in the same or in opposite senses, and two different kinds of hydrogen molecule result, known as *ortho*-hydrogen and *para*-hydrogen, respectively. It had been shown by Dennison (1927) that the curves representing the specific heat of hydrogen at low temperatures, which previously offered great theoretical difficulties, could be explained on the assumption that ordinary hydrogen is a mixture of these two kinds of molecules in the ratio of 3 to 1. Evidence of the existence of these in liquid hydrogen was found by an optical method by McLennan and McLeod early in 1929. In 1929, Bonhoeffer and Harteck found that ordinary (*ortho*-) hydrogen is converted into the other modification, *para*-hydrogen, by pressure and cooling. At 350 atm. pressure and liquid air temperature, the conversion is complete in a week. Pure *para*-hydrogen melts at 13·83° abs., ordinary hydrogen at 14 1° abs. Absorption on charcoal at liquid air temperature gives practically pure *para*-hydrogen. The two

modifications, which exist as gases, are said to have slightly different vapour pressures.

Isotopes of hydrogen.—Two isotopes of hydrogen, H^1 and H^2, of masses 1·0077 and 2·0135, have been detected spectroscopically and by the mass spectrograph, the relative abundance in ordinary hydrogen being 30,000 1. The heavier isotope increases in proportional amount during the prolonged electrolysis of water, and in this way water $H_2{}^2O$, of density 1·1056 at 25°, freezing point +3·8° and boiling point 101·42°, has been obtained (Urey, 1932, G N Lewis, 1933).

The occlusion of hydrogen by metals.—Deville observed that platinum and iron become permeable to hydrogen at a red heat, and concluded that "metals and alloys have a certain porosity." Graham (1866–69) 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 at 245° in a vacuum.

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 suggested that hydrogen was the vapour of an exceedingly volatile metal, **hydrogenium**. This hypothesis was disproved when solid hydrogen was shown to be a transparent, glassy solid, 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. 10.—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 often continues to come off slowly from the cathode, showing that the metal had become *supersaturated* with hydrogen. If the current is then 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. The palladium strips bend, owing to the unequal expansion on absorption of hydrogen

Troost and Hautefeuille (1874) pumped off hydrogen occluded in palladium, and measured the pressures during its removal at a given temperature. The first portions came off readily, but when 600 vols. of hydrogen were left to 1 vol. of palladium, the rest of the gas came off at a constant pressure, as does water vapour from a salt containing water of crystallisation (p. 169). Hence these observers concluded that a definite **hydride of palladium** was present Constant pressure intervals were observed at different temperatures.

The density of palladium is 12, hence the ratio of the weights of palladium and hydrogen in the metal which has occluded 633 vols of hydrogen is $12 \cdot 633 \times 0\ 00009 = 12 : 0{\cdot}057$. The atomic weight of Pd is 106, hence the ratio of the atoms in palladium saturated with hydrogen is

$$\frac{12}{106}\ 0\ 057 = 2\ 0\ 1,$$

corresponding with Pd_2H.

Roozeboom and Hoitsema (1895) repeated the investigations of the two French chemists. They considered that the pressure curves in the dissociation of the "palladium hydride," at temperatures between 0° and 190°, consisted of *three* parts (Fig. 89): two rapidly ascending portions, joined by a nearly horizontal but slowly rising middle portion. At higher temperatures the flat part became appreciably shorter. It was less flat if palladium black was used instead of foil.

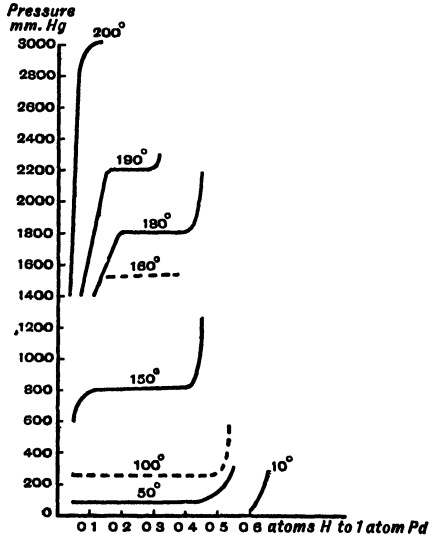


FIG. 89.—Palladium and hydrogen curves.

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 solid solutions. The flat part, where the pressure is practically constant, indicates that *two* solid solutions must be present. Since the pressure depends only on the temperature, the Phase Rule gives $F=1$; $C=2$; $\therefore P=3$, *i.e.*, gas + 2 solids.

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 concluded that the hydrogen exists partly as a condensed layer on the surface, and partly dissolved in the interior of the metal, and not usually homogeneously distributed.

They found that palladium is normally inactive but 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 The absorption of gas is at first rapid, then becomes increasingly slower. 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°.

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 is not homogeneously distributed throughout the metal The surface layer is easily removed by pumping, the gas in the interior is much more firmly held.

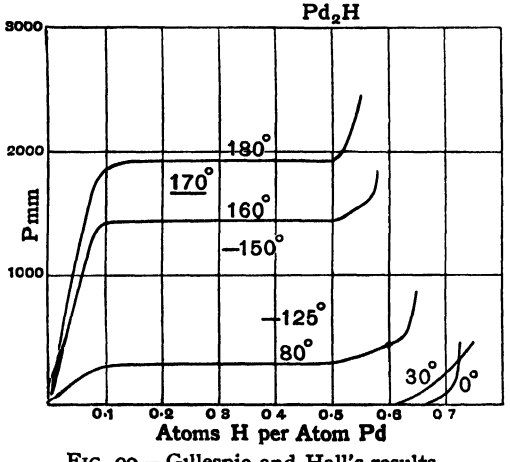


FIG. 90.—Gillespie and Hall's results

Gillespie and Hall (1926) took extra precautions to obtain states of true equilibrium, using very finely divided palladium and special heat treatment. They obtained perfectly horizontal isotherms (Fig. 90) and found evidence of two immiscible solid solutions, but at temperatures of 80°, 160° and 180° the one richer in hydrogen had practically the composition

of a palladium hydride Pd_2H or Pd_4H_2, which is regarded as a definite compound, separating nearly pure at these higher temperatures, but at lower temperatures dissolving increasing amounts of hydrogen.

A. W Porter (1918) remarked 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 gases do not react at the ordinary temperature, a jet of hydrogen is inflamed if directed on a little platinum sponge. The same effect is produced by a bundle of fine platinum wires which are perfectly clean; these become red-hot and then kindle the hydrogen (Dobereiner, 1823). It is not shown by metals such as iron or copper, and in this case, therefore, the platinum exerts a specific **catalytic action.**

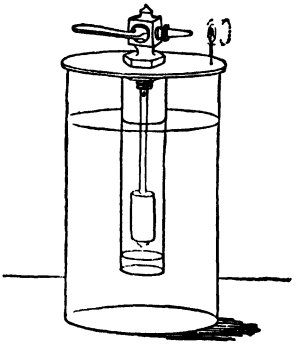


FIG 91—Dobereiner's lamp

Dobereiner's lamp (Fig. 91) is a small hydrogen generator, composed of a glass tube immersed in dilute sulphuric acid, with a stopcock and jet at the top. A piece of zinc hangs inside the tube, 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.

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:**

(1) Faraday considered that both the gases formed a *condensed film* on the metal surface as a result of the action of surface-forces of the solid. 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 and Marcet (1828) 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.

According to Faraday, platinum does not catalyse the union of hydrogen and chlorine He also found that the catalytic activity of a clean platinum surface was arrested when a small quantity of carbon monoxide was added to the mixture of hydrogen and oxygen, but the metal recovered its activity when brought into a gas mixture free from carbon monoxide The presence of traces of hydrogen sulphide in the gas " poisoned " the platinum so that it did not become active again until it had been boiled in concentrated sulphuric acid.

Graham in 1868 suggested that gas films formed by *adsorption* on metals might contain the gas molecules *orientated* in a particular direction, so that the same part of the molecule would always be in contact with the metal, and the other part exposed as a film to the gas space

Later investigations, notably by Langmuir, indicate that the adsorbed layer is unimolecular in thickness, that it is generally orientated, and that " poisoning " is due to the formation of films of molecules which prevent the adsorption of gases otherwise capable of reacting on a clean surface In some cases (*e g*, with carbon monoxide) these films may evaporate again in a pure gas Langmuir supposes that the adsorbed molecules are held by attractive forces analogous to residual affinity, which originate in the atoms of metal lying on the surface, these possessing uncompensated attractions, whereas the metal atoms inside the mass have no residual attractions, since they are completely surrounded by other atoms He looks upon a metal surface as something like a chess-board, the black spaces being metal atoms and the white spaces the spaces between the atoms. Molecules of gas are held by the spaces occupied by metal atoms The catalytic action may take place by interaction between molecules or atoms held on adjacent surface atoms of metal, or between an adsorbed film and the atoms of the solid, or directly as a result of a collision between a gas molecule and a molecule or atom held on the surface Reaction between hydrogen and oxygen, he considers, occurs between adjacent adsorbed atoms, that between carbon monoxide and oxygen between oxygen atoms, formed from adsorbed oxygen molecules, and colliding carbon monoxide molecules The products of reaction then evaporate from the surface. In the case of adsorption of gases on salt crystals, Haber (1914) considers that the molecules are held by electrical forces from the positive and negative ions of the salt in the surface of the crystal.

CHAPTER XII

WATER

The physical properties of water.—Water exists in three states : solid (ice), liquid (water), and vapour (steam). Steam consists almost wholly of H_2O molecules There are several varieties of ice, and liquid water probably contains polymerised molecules $(H_2O)_n$.

Liquid water possesses a faint though distinct blue colour (the colour of liquid oxygen is blue), 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 shows the same colour in large masses, as in crevices of glaciers or icefloes The deep blue colour of some clear lakes appears to be due to light scattered from fine particles of solid matter in suspension.

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 . at 3·98° water is in a state of **maximum density**. 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 1000·028 cm.^{3}. The volume of 1 kgm. of water at 15°, weighed *in air*, is **Mohr's litre** ; it occupies 1001·98 cm.^{3}

The density of ice at 0° is 0·9168 ; it floats on water, which expands on freezing. The liquid may be supercooled to about −4°. 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 burst when immersed in a freezing mixture.

The **densities of water**, referred to the weight in grams of one-thousandth of a standard litre (1 ml) at 4° as unity, are as follows :

−5°	0·99930	8°	0 999808	100°	0·9584
0°	0·99987	10°	0·99973	150°	0·9173
4°	1·00000	20°	0·99823	250°	0·794

The amount of heat required to raise the temperature of 1 gm. of water from 14½° to 15½°, *i.e.*, through 1°, is called the **gram calorie**

(g. cal.). This varies slightly with the temperature of the water; at 0° and 100° it is slightly greater than at 15°. The corresponding amount for 1 kilogram of water is the **kilogram calorie**: 1 k. cal. = 1000 g. cal. This heat may be generated by stirring the water, and the number of units of work spent in generating 1 g cal. is the **mechanical equivalent of heat**, $4{\cdot}184 \times 10^7$ ergs per 15° g. cal.

The number of g. cal. required to raise the temperature of 1 gram of a substance through 1° under specified conditions is the **specific heat**: 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 79·74 g. cal. per gram of ice, is the **latent heat of fusion** of ice (or **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 539·1 g. cal., called the **latent heat of evaporation** of water (or the **latent heat of steam**) For evaporation at other temperatures it possesses different values. 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 corresponds with the formula H_2O. When this is corrected for deviations from Boyle's laws the results show that little, if any, association exists in the vapour (the experimental results are conflicting) and that steam consists almost entirely of H_2O molecules (**hydrone**, or **hydrol**). The properties of liquid water, its high surface tension, high dielectric constant and great tendency to promote ionisation of dissolved electrolytes, as well as its abnormal physical properties (high boiling point as compared with hydrogen sulphide, H_2S), the expansion on solidification, and the existence of a maximum density above the freezing-point, all seem to point to an association of H_2O molecules in the liquid. The existence of $(H_2O)_2$ molecules in equilibrium with H_2O molecules in the liquid: $(H_2O)_2 \rightleftharpoons 2H_2O$, and, to explain the anomalous expansion of liquid water below 3·98°, the presence of $(H_2O)_3$ molecules, have been assumed, the latter being formed from H_2O molecules by expansion, and present in water near the freezing point. Another hypothesis assumes the presence of $(H_2O)_6$ molecules, with simple H_2O molecules, in the liquid.

The X-ray examination of ice indicates, according to Sir W. H Bragg, that the individuality of the H_2O molecule is lost in the crystals, these molecules being broken up into positively and negatively charged atoms (ions), H^+ and O^{--}, arranged in a hexagonal lattice in which each oxygen atom is surrounded by four other oxygen atoms, from each of which it is separated by an atom of hydrogen, and each hydrogen atom is therefore between two atoms of oxygen. The structure is very empty, and a loose arrangement of H_2O molecules might occupy less space; hence pressure would tend to melt the ice. This arrangement

gives the hexagonal crystal form and low density of ice. Other results indicate that ice contains molecules, not ions.

There are, however, different **varieties of ice**, formed from ordinary ice under high pressures (Tammann ; Bridgman).

Ordinary ice, **ice I**, is in equilibrium with water vapour and liquid water at +0·0077° C. under a pressure of 4·579 mm. It is always produced when water crystallises spontaneously under pressures less than 2,500 kgm./cm.^{2} Above this pressure **ice III** or **ice II** forms ; between pressures of 3,500 and 6,300 kgm./cm.^{2} ice II or **ice V** is produced, according to the temperature ; under higher pressures **ice VI** is formed. Ice II ($d = 1·03$) cannot exist in equilibrium with liquid water. Ice I, ice II and ice III ($d = 1·04$) exhibit a triple point at −34·7° C. and 2,170 kgm./cm.^{2} ; ice II, ice III and ice V ($d = 1·09$) are in equilibrium at −24·3° C. and 3,510 kgm./cm.^{2}. The existence of **ice IV** is doubtful ; ice VI ($d = 1·06$) is stable only at temperatures above 0° C. Ice II and ice III differ in space lattice only.

The vapour pressures of ice are slightly less than those of supercooled liquid water at the same temperatures. Water cooled below 0° freezes in contact with ice or if violently agitated, and the temperature rises to 0°. 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 raised above 100°, the temperature of saturation, by passing through heated tubes.)

Ice crystallises in the hexagonal (six-sided) system (Fig. 92). The bubbles in ice are composed of air dissolved in the water, and 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.

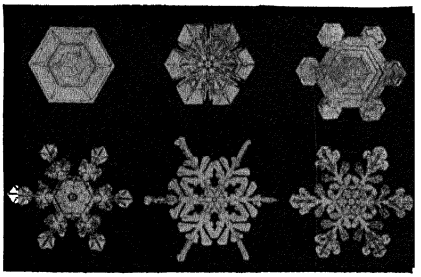


FIG. 92.—Snow crystals.

Efflorescence. — Definite solid chemical compounds of salts with water are called **hydrates.** White anhydrous copper sulphate at once becomes blue if water is poured on it, and heat is evolved. On cooling a hot solution of copper sulphate in water, deep blue crystals of the hydrate, $CuSO_4,5H_2O$, called *blue vitriol*, separate out. If exposed to dry air in a desiccator over sulphuric acid, they fall to a nearly white powder of the monohydrate, $CuSO_4,H_2O$, which again becomes blue when moistened with water.

Some crystalline hydrates lose water and fall to powder on exposure to the atmosphere. This change, called efflorescence, shows that there

must be a pressure of water vapour over the salt, and this is confirmed by passing a crystal of the salt above the mercury in a barometer tube, when the mercury falls slightly. The vapour pressure 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.

The system has two components, viz., anhydrous salt and water. Since the vapour pressure depends only on the temperature, there is only one degree of freedom; hence the Phase Rule, $P+F=C+2$, shows that the number of phases is: $2+2-1=3$. These are water vapour and *two* solids. One solid is the original hydrated salt, the second is either 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 the vapour pressure above the hydrated salt at the ordinary temperature is greater than the partial pressure of water in the atmosphere, the salt will lose water on exposure and will effloresce. If, on the other hand, the pressure over the salt is not greatly different from that of atmospheric moisture, the crystals will be stable on exposure. Blue vitriol does not effloresce on exposure, since the vapour pressure over its crystals at 25° is only 7·92 mm., whilst the partial pressure of atmospheric moisture, usually about two-thirds the saturation pressure at the given temperature, is about 15 mm. If the vapour pressure over the hydrate is very small, it may absorb moisture from the air. Ordinary granular calcium chloride used for drying gases, $CaCl_2,2H_2O$, has a very small vapour pressure, and absorbs moisture from gases, forming $CaCl_2,6H_2O$.

The name efflorescence first denoted the "creeping" of solutions of salts in open vessels, with the formation of a loose deposit on the sides of the vessel. This action is no doubt caused by the formation of crystals on the walls at the surface of the liquid, which then rises by capillary action between the crystals or between these and the wall of the vessel. More crystals are thus formed above the first layer, and so on, until in some cases the solid reaches to the top of the vessel, when the solution may siphon over and creep down the outside of the vessel. This occurs with salammoniac solutions in Leclanché cells and may be prevented by greasing the upper part of the jar.

Vapour pressures of hydrates.—The definite vapour pressure over a hydrated salt, as compared with the variable pressure over a solution, enables us to distinguish between the two cases. A mechanical mixture of liquid water with a solid has a vapour pressure equal to that of pure water, provided a solution is not formed. A hydrate containing hygroscopic moisture, 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, say $CuSO_4,5H_2O$, and the pressure falls to A (Fig. 93). Dissociation of this hydrate then begins: $CuSO_4,5H_2O \rightleftharpoons CuSO_4,3H_2O + 2H_2O$, and 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 $CuSO_4,5H_2O$, is converted into $CuSO_4,3H_2O$, and the pressure again falls abruptly to a lower value, C.

Dissociation into $CuSO_4,H_2O$ now begins: $CuSO_4,3H_2O \rightleftharpoons CuSO_4,H_2O + 2H_2O$. This hydrate has a very small vapour pressure,

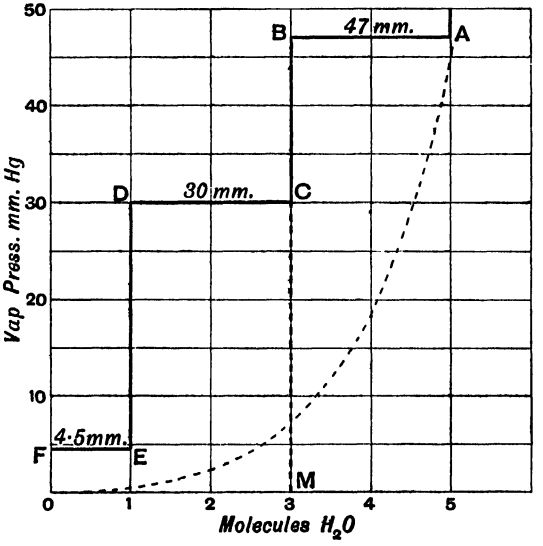


FIG. 93 —Vapour pressure curves for dissociation of a series of hydrates of copper sulphate at 50°.

but gives off water in a desiccator over phosphorus pentoxide, forming the anhydrous salt. When all the trihydrate is converted into the monohydrate, the pressure falls sharply to a low value, E, and remains at this pressure until all the water is removed; it 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 hydrates may be found.

The dotted curve AO' represents the vapour pressure of a solid solution (*e.g.*, jelly), which loses water continuously.

Natural waters.—The following division of natural waters is convenient: (1) **rain**, (2) **river**, (3) **spring**, or **deep well**, (4) **sea** and (5)

mineral. The impurities in natural water are of two kinds: (1) *suspended*, both mineral and organic; (2) *dissolved*, 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 deposited near, or in, 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 as ammonium nitrite and nitrate, and sometimes free ammonia occurs. In towns, sulphuric acid, from the combustion of coal (which contains iron pyrites, FeS_2), is present. Suspended impurities, chiefly soot from fuel smoke, are usually contained in rain The free sulphuric acid may be neutralised by 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 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 unstable soluble bicarbonates These are readily decomposed on boiling the water, with precipitation of the insoluble carbonates and evolution of carbon dioxide

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2, \quad MgCO_3 + H_2CO_3 \rightleftharpoons Mg(HCO_3)_2$$

EXPT 1.—Pass a stream of carbon dioxide (washed from acid spray by passing through a wash-bottle containing water) into lime-water This 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: $Ca(HCO_3)_2$, (or $CaO,2CO_2 + H_2O$, *i.e.*, containing *twice* as much CO_2, for the same weight of lime, as the carbonate, CaO,CO_2) On boiling, the clear liquid again becomes turbid, and calcium carbonate is precipitated. The reaction is reversible · $CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$ If an equal volume of lime-water is added to the clear bicarbonate solution, turbidity is produced, and nearly insoluble calcium carbonate precipitated · $Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$ (or, omitting water: $CaO,2CO_2 + CaO = 2CaO,CO_2$). The filtrate is practically free from calcium salts.

Hard and soft waters.—The presence in water of bicarbonates of calcium and magnesium produces what is called **temporary hardness**; such water destroys soap without producing a lather, but is "softened" by boiling.

A method of softening water is Gans' **permutit process.** Permutit is a silicate of sodium and aluminium allied to the natural mineral zeolites On percolating hard water through it, the calcium and magnesium salts are removed and replaced by an equivalent of sodium salt The change is reversible, and the permutit may be re-activated by percolation with a solution of common salt A permutit containing manganese dioxide oxidises dissolved iron and manganous salts, which are injurious in laundering, etc , precipitating the oxides

The different varieties of hard soap consist of the sodium salts of organic acids derived from fats. Soft soap consists of the potassium salts of these acids. These salts are soluble in water, and are *slightly* decomposed by the latter, giving caustic soda and an acid soap. *E.g.*, with sodium palmitate :

$$2C_{15}H_{31}CO_2Na + H_2O \rightleftharpoons (C_{15}H_{31}CO_2)_2HNa + NaOH.$$

This decomposition of a salt by water, with production of free acid and base, is called **hydrolysis.** The soap in solution considerably lowers the surface tension of water, so that soapy water readily froths, and particles of dirt tend to accumulate in the liquid. The **detergent action** of soap is thus an instance of separation by surface tension effects.

EXPT. 2 —Shake paraffin oil with distilled water · an emulsion is formed, but rapidly separates again into two layers Add a little soap solution, and shake vigorously. A more stable emulsion is formed The detergent action of soap depends on its property of emulsifying grease in this way ; the fine droplets can then be washed away with water.

EXPT. 3.—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 in a 1 per cent soap solution 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 insoluble calcium and magnesium salts of the fatty acids

$$CaCO_3 \text{ (dissd)} + 2NaCO_2{\cdot}C_{15}H_{31} = Ca(CO_2\,C_{15}H_{31})_2 \text{ (ppd.)} + Na_2CO_3.$$

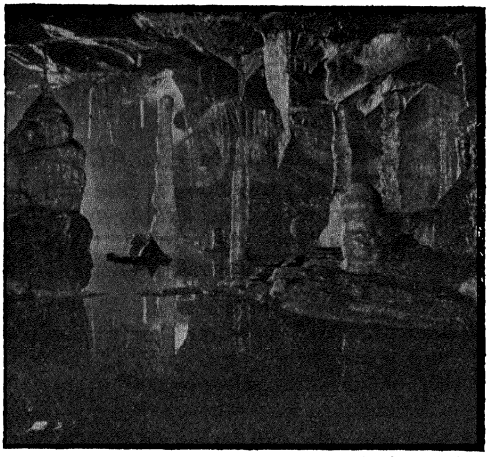
About 0·17 lb of soap is required for 100 gallons of water containing 1 grain of $CaCO_3$ per gallon, instead of 0·075 lb (theoretical) The slimy precipitate of calcium salts carries down with it some of the soap, and renders it useless It also adheres tenaciously to the skin or fabric, and interferes with washing. The hard 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 excess of the soap has been added.

Ferrous carbonate dissolves in water containing carbonic acid, forming ferrous bicarbonate, $Fe(HCO_3)_2$. On boiling, a reddish-brown

precipitate of hydrated ferric oxide 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 oxalic acid solution.



[*Photo. Frith & Co. Ltd.*

FIG. 94.—Stalactites and stalagmites in Cox's Cave, Cheddar.

Temporarily hard waters deposit a crust or scale of calcium carbonate when boiled in kettles or boilers, which 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. 94). 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 formed under brickwork arches, even in localities where the water is soft, are derived from the calcium carbonate in the mortar, which is dissolved by the carbon dioxide in rain.

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 :

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

When 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 magnesium hydroxide is much less soluble (0·01 gm. per litre). The precipitates are allowed to settle, and the softened water run off for use.

A different kind of hardness is due to sulphates or chlorides of calcium and magnesium, derived from the soil. These are not precipitated on mere boiling, and cause **permanent hardness.** The water may at the same time possess temporary hardness. If such waters are evaporated in boilers, calcium sulphate, $CaSO_4$, is deposited as a very hard crystalline scale, which may give rise to overheating of the metal. 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 may be 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, but sodium carbonate and sulphate remain in solution, so that this process is not used with drinking water

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4,$$
$$Ca(HCO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O.$$

In softening water for use in boilers, both lime and sodium carbonate, in special apparatus, are applied. The lime is first treated with part of the water to produce a clear lime water, which then mixes with the raw water, and a solution of sodium carbonate is at the same time added. The water, after some solid has deposited, then passes through a filter. The whole operation proceeds continuously

Other materials used on the small scale in laundering are: ammonia, which acts similarly to caustic soda, and borax, $Na_2B_4O_7,10H_2O$, which precipitates calcium borate, $Ca(BO_2)_2$, 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 usually 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 (parts per 70,000).

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, apocrenic and humic), some of which give it a yellow colour, and cause it to corrode lead or iron pipes.

River water flowing over cultivated land may contain, 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.

River water, like other natural waters, contains dissolved atmospheric gases, the oxygen of which is of importance to fish.

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, ammonia 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.

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, caesium, 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 several kinds:

(1) **Acidulous waters** contain dissolved carbon dioxide, together with alkali bicarbonates, and common salt. The carbon dioxide may be liberated with effervescence when the water is 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 bicarbonate. On exposure to air, such water deposits brownish-red ferric hydroxide. *E g.*, Pyrmont water.

(3) **Hepatic waters** (Latin *hepar*, liver), contain hydrogen sulphide, H_2S, and alkali sulphide, *e g*, Na_2S. They smell of hydrogen sulphide, and on exposure to air deposit sulphur: $2H_2S + O_2 = 2H_2O + 2S$. 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 silica and alkali silicates Such waters, *e g*, of the geysers of Iceland, New Zealand, and Yellowstone Park (America), are usually almost boiling, and deposit masses of siliceous sinter at the mouth of the geyser

(7) **Iodine water** contains dissolved iodides, and occurs at Woodhall Spa (Lincoln), and in Central Europe

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, to which their medicinal properties are attributed

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 of varying degrees of coarseness, the upper parts, of fine gravel, being removed and washed from time to time. The water is freely exposed to air so as to take up oxygen. Filter beds remove most of the bacteria from water. but for safety the water 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. Treatment with ozone is also used. A potable water should not usually contain any *Bacilli coli* in 100 c c.

Action of water on metals.—Potable water is conveyed through lead or iron pipes. Some waters passing through iron pipes lead to the growth of vegetation, which rapidly corrodes the iron, and 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. The action is due partly to dissolved oxygen, and partly to *free* carbonic acid. Hard water has much less action on lead than soft water.

EXPT. 4.—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 hydrogen sulphide 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*, in rain water) increases the action. Peaty waters, containing organic acids, act rapidly on lead or zinc, unless neutralised by lime

Pure water.—It is very difficult to obtain water in a state of extreme purity. 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.

The dissociation of steam.—When electric sparks are passed through steam, it is decomposed to a slight extent into hydrogen and oxygen: $2H_2O \rightleftharpoons 2H_2 + O_2$. The dissociation of steam by heat increases with the temperature The following table gives the percentage dissociation *i.e.*, the number of molecules decomposed out of every 100 molecules of steam.

$T°$ abs.	10 atm	1 atm	0·1 atm.	0·01 atm
1000	$1·39 \times 10^{-5}$	$3·00 \times 10^{-5}$	$6·46 \times 10^{-5}$	$1·39 \times 10^{-4}$
1500	$1·03 \times 10^{-2}$	$2·21 \times 10^{-2}$	$4·76 \times 10^{-2}$	0·103
2000	0·273	0·588	1·26	2·70
2500	1·98	3·98	8·16	16·6

At the melting point of platinum (1755°) and 760 mm. pressure, about 6 molecules of steam in every thousand are dissociated. At 7·6 mm. pressure this number increases to 27.

Water is also decomposed when the liquid is exposed to short-wave ultra-violet light. At first only hydrogen is evolved, the oxygen probably forming hydrogen peroxide: $2H_2O = H_2 + H_2O_2$. After a time oxygen is also evolved: $2H_2O_2 = 2H_2O + O_2$. Water is also decomposed by the α-rays from radium emanation.

The thermal 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 at 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.—Early experiments on the composition of water by volume are those of Cavendish (1781), who obtained the ratio H/O = 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.

An 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. 129), 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 Morley found 200·269 : 100.

A more recent determination of the ratio is that of Burt and Edgar (1915). The final result, the average of 59 determinations, was 200·288 : 100, agreeing with Scott's to within 3 parts in 200,000. The special points of the 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; it was dried by phosphorus pentoxide, and further purified. (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 containing palladium black to convert oxygen to 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 95) consisted of a 300 c.c. glass 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

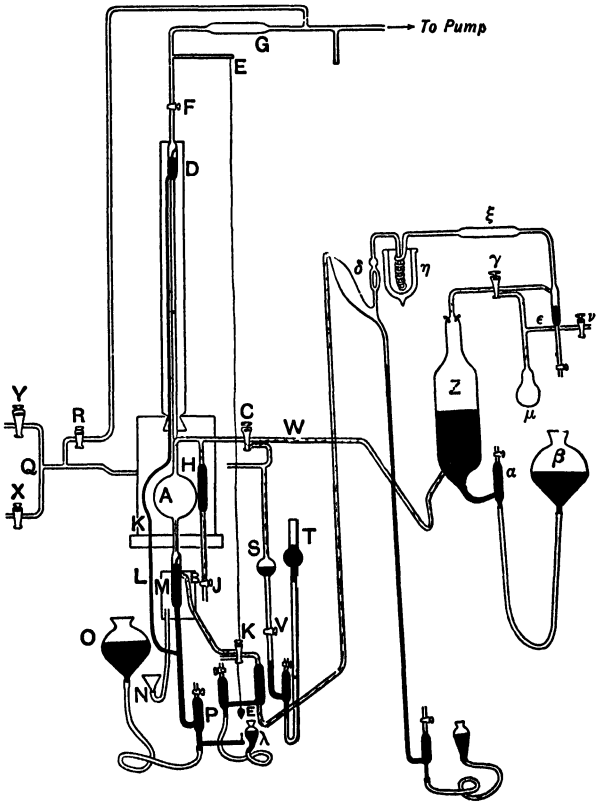


FIG 95 —Volumetric composition of water · apparatus of Burt and Edgar

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 that in the upper chamber, *D*, also provided with a levelling-point; 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 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 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, *J* From the weight of this mercury the volume of the residual gas was calculated.

From the results of these experiments 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, 0·089873 gm. and 1·42900 gm. respectively. With these figures, the values of Burt and Edgar give, for the weight of oxygen combining with 1 part by weight of hydrogen :

$$\frac{1{\cdot}42900}{2{\cdot}00288 \times 0{\cdot}089873} = 7{\cdot}9387.$$

The atomic weight of hydrogen is therefore :

$$8{\cdot}0000/7{\cdot}9387 = 1{\cdot}0077.$$

These results leave no doubt that the ratio of the atomic weights of hydrogen and oxygen cannot be expressed in terms of whole numbers, 1 : 16, as Dumas thought. This conclusion is important, since a whole number ratio was assumed by Prout in 1815 and made the basis of a hypothesis, according to which all atomic weights are whole multiples of that of hydrogen and consequently all atoms might be supposed to be formed by the condensation of atoms of hydrogen, looked upon as a primary substance. **Prout's hypothesis** in its original form has been disproved by experiment in a large number of cases, since the atomic weights of elements, when referred to hydrogen as unity, are not whole numbers. In a few cases the values when referred to oxygen as 16·000 are nearly whole numbers, but in the majority of cases they are not whole numbers on this standard.

CHAPTER XIII

COMMON SALT. HYDROCHLORIC ACID CHLORINE

Common salt.—After air and water, there is probably no material so familiar as common salt. It is an essential constituent of food, about 29 lb. per head of population being annually consumed in this way. In 1907 nearly 2,000,000 tons of salt were recovered from brine and rock-salt in Great Britain alone Common salt is contained in small quantities in 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 seawater 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

Rock-salt, or **halite**, is the crystalline variety, occurring in cubic crystals, colourless when pure, but often tinged yellow, brown, or sometimes blue, by impurities, or else in large more or less coloured masses, which have a cubic cleavage The richest English deposits are in the Cheshire district, at Northwich and Winsford, in the Upper Trias formation.

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.

The densities of salt solutions at 15° are :

% salt	2	5	10	15	20	25	26·8
Density	1·0137	1·0355	1 0726	1·1105	1·1497	1·1904	1 2055

From 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 sent 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. 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) In some works the brine is evaporated in vacuum pans under reduced pressure. These are iron boilers heated by steam coils (Fig. 96), 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

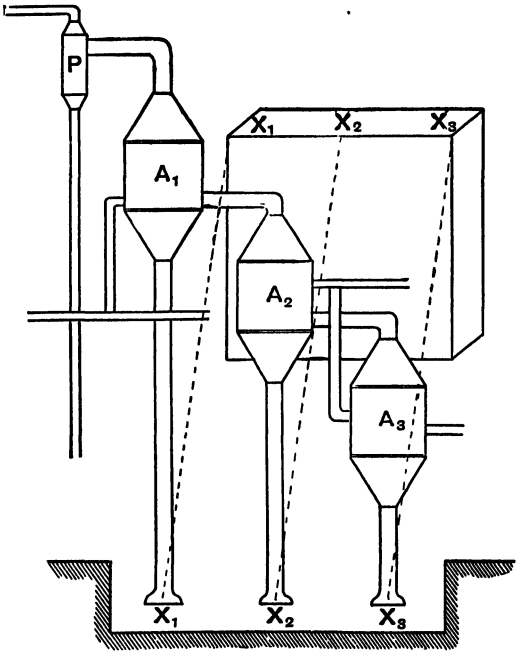


FIG 96 —Vacuum evaporation pans

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 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. Large quantities are used in producing alkalies, viz. sodium carbonate and caustic soda, and chlorine Salt is used in preserving fish and other foods, in glazing common earthenware such as drain-pipes, and in melting snow and ice on roads, an effect due to the lowering of freezing point of water by the dissolved salt (p. 85). In salt-glazing, 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 : $SiO_2 + 2NaCl + H_2O = Na_2SiO_3 + 2HCl$

The history of chlorine.—In 1648 Glauber obtained a strongly acid **spirit of salt** by heating moist salt in a charcoal furnace and condensing the fumes in a receiver. A mixture of salt, alum and copperas (ferrous sulphate) heated in the furnace gave a better yield, and a product of the reaction was **Glauber's salt,** sodium sulphate, $Na_2SO_4,10H_2O$ In 1658 Glauber (in his *De Natura Salium*) obtained spirit of salt by distilling salt with concentrated sulphuric acid and condensing the vapours in water. Boerhaave (1732) calls the concentrated solution so prepared *spiritus salis Glauberi*. 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, a word used by Cicero). 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. 37), this amounts to the same thing as muriatic acid deprived of hydrogen. Muriatic acid—H. This is correct.

In 1785 Berthollet found that a solution of the new gas in water, when exposed to light, 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 acid, which was a difficulty.

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, phosphorus 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 usually 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 and gaseous hydrogen chloride, in the presence of a heated copper salt acting as a catalyst or carrier of oxygen, may be used; or a solution of the acid may be treated with a substance rich in oxygen which readily parts with that element, such as manganese dioxide, MnO_2; potassium permanganate $KMnO_4$; potassium dichromate, $K_2Cr_2O_7$; and bleaching powder, $CaOCl_2$.

The reaction between gaseous hydrogen chloride and oxygen in presence of the catalyst is: $4HCl + O_2 = 2H_2O + 2Cl_2$.

EXPT. 1.—A stream of air is passed through concentrated sulphuric acid in a Woulfe's bottle, and concentrated hydrochloric 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. 97) to a dull red heat. The gas is then passed through litmus solution, which is rapidly bleached by the chlorine evolved. The copper sulphate is first converted into chloride.

$$CuSO_4 + 2HCl = CuCl_2 + H_2O + SO_3.$$

The oxidation by means of manganese dioxide also occurs with gaseous hydrogen chloride, and takes place very slowly in the cold but

rapidly on heating. In this case no free oxygen is required, as the oxygen needed is provided by the manganese dioxide:

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

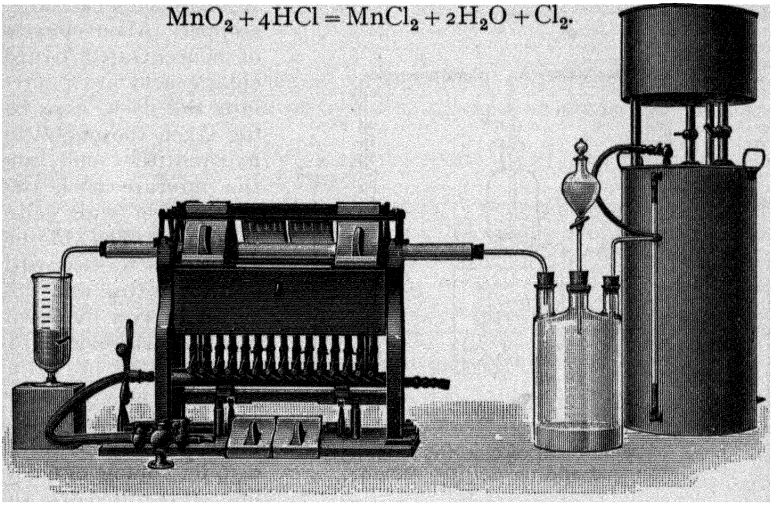


FIG. 97.—Oxidation of hydrochloric acid gas by atmospheric oxygen with formation of chlorine.

EXPT. 2.—Place powdered manganese dioxide in one bulb of a hard glass tube, leaving the other bulb empty. Pass a slow current of hydrogen chloride, obtained by dropping concentrated hydrochloric acid into concentrated sulphuric acid in the apparatus of Expt. 1, over the dioxide, and allow the gas to pass into a bottle containing litmus solution and a piece of moist red flannel (Fig. 98). Heat the manganese dioxide. Moisture collects in the second bulb, and chlorine passes on to the bottle and bleaches the litmus and the red flannel.

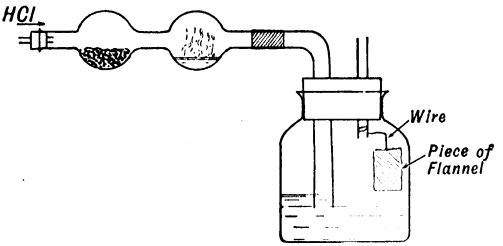


FIG. 98.—Oxidation of hydrochloric acid gas by heated manganese dioxide.

The usual laboratory method of preparing chlorine is to decompose aqueous hydrochloric acid with manganese dioxide: the mineral form called *pyrolusite*, in small pieces, is most convenient.

EXPT 3.—About 100 gm of pyrolusite in small pieces are placed in a two-litre flask fitted with a long thistle funnel and delivery tube through a black rubber stopper About 300 c c. of concentrated hydrochloric acid are poured into the flask, care being taken thoroughly to moisten the solid, and the mixture is heated gently over wire gauze (Fig 99). The chlorine evolved is washed with a little water and collected in jars by downward displacement (it is 2½ times as heavy as air) It may also be collected over saturated brine, which dissolves 0 36 its volume of chlorine If required dry, the gas is passed through concentrated sulphuric acid in a second wash-bottle The preparation is carried out in a good draught cupboard, as the gas has a powerful corrosive action on the mucous membranes The inhalation of alcohol vapour, and diluted ammonia gas, relieves the bad effects produced by breathing air containing chlorine

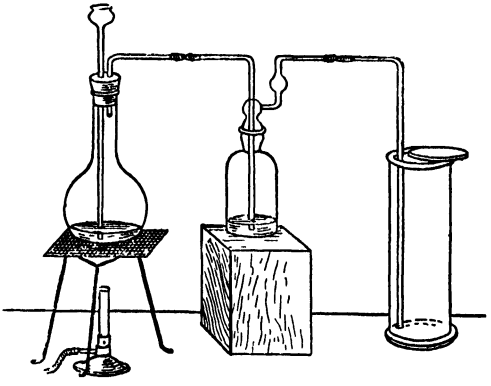


FIG 99 —Preparation of chlorine from hydrochloric acid and manganese dioxide

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

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O\ ;$$
$$MnCl_4 = MnCl_2 + Cl_2$$
$$2MnO_2 + 8HCl = 2MnCl_3 + Cl_2 + 4H_2O\ ;$$
$$2MnCl_3 = 2MnCl_2 + Cl_2$$

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). $4NaCl + MnO_2 + 3H_2SO_4 = Cl_2 + 2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O$.

Potassium dichromate readily oxidises hydrochloric acid on heating :

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2.$$

EXPT. 4.—The 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.

A very convenient method of obtaining small amounts of pure chlorine is by the action of hydrochloric acid on potassium permanganate:

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

EXPT 5.—Drop concentrated hydrochloric acid slowly on crystals of potassium permanganate in a flask. Chlorine 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. By passing this gas through a glass bulb cooled in solid carbon dioxide and ether, liquid chlorine is formed, by the evaporation of which almost perfectly pure chlorine may be obtained.

If concentrated hydrochloric acid is dropped on bleaching powder in the above apparatus, chlorine is evolved. $CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2$

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 dilute hydrochloric acid.

Pure chlorine may be obtained by heating dry platinic chloride, $PtCl_4$, or auric chloride, $AuCl_3$ (gold chloride) in a hard glass tube. Platinous, or aurous, chlorides are first produced, which decompose, giving the metals, at higher temperatures:

$$PtCl_4 \overset{374^\circ}{=} PtCl_2 + Cl_2 \overset{582^\circ}{=} Pt + 2Cl_2.$$

$$2AuCl_3 \overset{175^\circ}{=} 2AuCl + 2Cl_2 \overset{185^\circ}{=} 2Au + 3Cl_2$$

Dry cupric chloride $CuCl_2$, when heated at about 350°, begins to decompose into cuprous chloride and chlorine: $2CuCl_2 = Cu_2Cl_2 + Cl_2$. The decomposition is rapid at 500°. 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 gaseous oxygen 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. Another set of reactions proposed involves the formation and decomposition of an oxychloride of copper :

$$2Cu_2Cl_2 + O_2 = 2Cu_2OCl_2, \quad Cu_2OCl_2 + 2HCl = Cu_2Cl_2 + H_2O + Cl_2.$$

It may be assumed 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 :

$$2H_2O \leftarrow O_2 \quad \begin{matrix} \leftarrow H & Cl \rightarrow \\ \leftarrow H & Cl \rightarrow \end{matrix} Cu_2Cl_2 \rightarrow 2CuCl_2 \rightarrow Cu_2Cl_2 + Cl_2$$

$$\begin{matrix} \leftarrow H & Cl \rightarrow \\ \leftarrow H & Cl \rightarrow \end{matrix} Cu_2Cl_2 \rightarrow 2CuCl_2 \rightarrow Cu_2Cl_2 + Cl_2$$

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 3·214 gm. per litre. The relative density at S T P is therefore 36·03 (O = 16). The relative density calculated from the atomic weight is 35·46, 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 normal up to 1200° 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 Crafts (1880) obtained the same result by displacing oxygen by chlorine, or chlorine by oxygen, in a porcelain apparatus at 1350° According to Victor Meyer and Langer (1885), at 1400° the density of chlorine fell to 29·29, which would correspond with a 21 per cent dissociation into atoms $Cl_2 \rightleftharpoons 2Cl$ Pier (1908), from specific heat measurements, assumed a dissociation of Cl_2 above 1450°, but the value given by Victor Meyer and Langer appears to be too high At very low pressures the dissociation is appreciable at 700°–900° (Henglein, 1922)

Chlorine, when cooled in solid carbon dioxide and ether, condenses to an amber-yellow liquid, boiling at −34·5°. On cooling in liquid air, this forms a pale yellow solid, melting at −100·9°. The critical temperature of chlorine is 140·9° ; its critical pressure is 76·1 atm. The gas is liquefied at 0° by a pressure of 3·66 atm. ; at 20°, 6·57 atm. pressure is required.

The chemical properties of chlorine.—Chlorine is a very active element ; it readily combines directly with hydrogen, and with most metals and non-metallic elements except nitrogen, oxygen, and carbon. Reaction often occurs when the elements are brought together at the

ordinary temperature, frequently with the production of flame, or incandescence.

The reaction with metals does not always take place if the chlorine is dry, although pure dry mercury completely absorbs pure dry chlorine. T. Andrews (1842) found that dry copper and zinc do not react with dry chlorine. Reaction between dry materials occurs in the cases of arsenic, antimony, mercury and phosphorus. Bromine behaves similarly Sodium may be melted in dry chlorine without reaction taking place (Wanklyn, 1883). In the following experiments, therefore, undried chlorine is to be used.

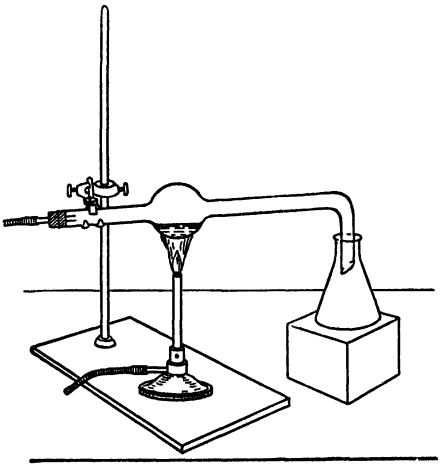


FIG 100 —Combustion of sodium in chlorine

EXPT 6 —Sprinkle a little finely powdered arsenic and antimony into jars of chlorine The substances burn, producing poisonous fumes of the chlorides $AsCl_3$, and $SbCl_5$

EXPT 7 —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 8 —Pass chlorine over a piece of sodium heated in a hard glass bulb tube (Fig 100) When strongly heated, the metal burns with an exceedingly brilliant yellow flame, producing sodium chloride, NaCl

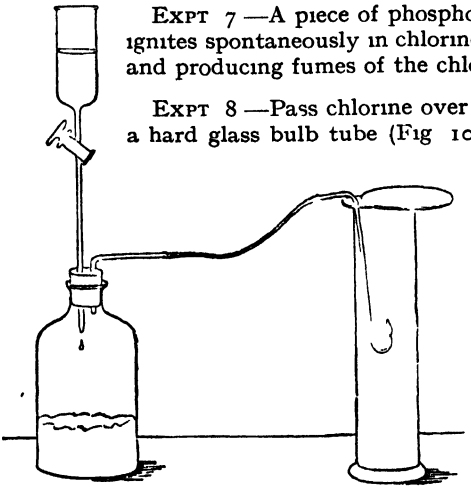


FIG. 101.—Combustion of hydrogen in chlorine

EXPT 9 —A jet of hydrogen burning in air continues to burn, with an enlarged greenish flame, when introduced into a jar of chlorine (Fig 101), producing hydrogen chloride

$$H_2 + Cl_2 = 2HCl.$$

A jet of chlorine burns when

introduced into an inverted jar of hydrogen which is burning at the mouth.

EXPT. 10.—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 In moist chlorine bleaching occurs.

EXPT 11 —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 Paraffin wax is a mixture of hydrocarbons, the chlorine removes the hydrogen, forming HCl, and sets free the carbon, with which it does not combine directly

EXPT 12 —A mixture of 2 vols of chlorine and 1 vol of ethylene C_2H_4, when ignited, burns with a red flame, emitting dense black clouds of carbon $C_2H_4 + 2Cl_2 = 2C + 4HCl$

EXPT 13 —A mixture of 2 vols of chlorine and 1 vol of methane 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 14 —A little turpentine, $C_{10}H_{16}$, boiled 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 directly 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 with chlorine on exposure to light, an oily liquid being formed.

Chlorine water.—Chlorine is fairly soluble in water, 2·68 volumes of the gas dissolving in 1 volume of water at 15°. The volumes of chlorine, reduced to S.T.P., dissolved by 1 volume of water are:

0°	10°	15°	20°	25°	30°
4 61	3·095	2·635	2·260	1·985	1 769

Below 9·6° the saturated solutions are metastable, being supersaturated with respect to the solid chlorine hydrate, in presence of which the solubility has a maximum value, 2·98, at 9·6°. In the figures given, it is assumed that the *total* pressure (chlorine + water vapour) is 1 atm. The solution, which may be prepared by passing chlorine through water in Woulfe's bottles, is pale yellow in colour, smells strongly of the gas, and 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 $2H_2O + 2Cl_2 = 4HCl + O_2$ In diffused daylight some chloric acid is also formed $5Cl_2 + 5H_2O = HClO_3 + 9HCl + O_2$.

Chlorine is less soluble in salt solution than in pure water, but it is more soluble in concentrated hydrochloric acid than in water, perhaps on account of the formation of a compound HCl_3.

Chlorine hydrate.—If chlorine is passed into water cooled in ice, almost white 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), $Cl_2,7H_2O$ (de Forcrand, 1902) and, according to Bouzat and Azinières (1923), $Cl_2,6H_2O$ if prepared in presence of liquid chlorine. 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 15.—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 102), liquid chlorine distils into the cooled part of the tube when the other is warmed to about 30°. These tubes must not be exposed to light for any length of time, otherwise oxygen is formed, which bursts them.

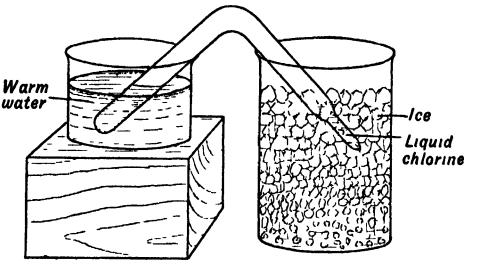


FIG 102.—Liquefaction of chlorine

Hydrogen chloride, or hydrochloric acid.—Chlorine and hydrogen form only one stable compound, hydrogen chloride, or hydrochloric acid, HCl. This occurs in some volcanic gases and in rivers near volcanoes. It is also found, to the extent of 0·2 to 0·4 per cent., in the gastric juice in normal conditions; in the dog's gastric juice as much as 3 per cent is present.

Hydrogen chloride is formed (Expt. 9) by the combustion of hydrogen in chlorine: $H_2 + Cl_2 = 2HCl$, and is produced technically in this way. It is usually prepared in the laboratory by heating common salt with concentrated sulphuric acid in a flask. The complete reaction

(1) $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$ requires a higher temperature than can be attained in glass apparatus and is achieved only on the technical scale (p. 201). At moderate temperatures the reaction proceeds mainly according to the equation (2) $NaCl + H_2SO_4 = NaHSO_4 + HCl$, so that the yield corresponds with about 70 per cent of equation (1). The hydrogen of sulphuric acid can thus 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.**

EXPT 16.—25 gm. of dry common salt are placed in a 500 c.c. flask, and covered with 25 c.c. of concentrated sulphuric acid. 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 (Fig. 99). It may be collected over mercury. When the jar is full of gas dense white fumes issue from the mouth, 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. The gas should not be dried by phosphorus pentoxide, as this slowly absorbs it, 227 c.c. of dry gas being taken up by 1 gm. of pentoxide: $2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$.

A convenient method of obtaining the gas is to use a Kipp's apparatus charged with concentrated sulphuric acid and lumps of salammoniac or a regular stream of gas is evolved.

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, an aqueous solution of the acid—*spirit of salt*—is produced. Each bubble of gas dissolves 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 formed by the action of concentrated sulphuric acid on other metallic chlorides, such as potassium, ammonium, magnesium and calcium chlorides, but lead, silver, cuprous, mercuric and mercurous chlorides are acted upon only with difficulty, if at all.

Hydrogen chloride is formed by the action of water on the chlorides of boron, aluminium, silicon and phosphorus (carbon tetrachloride, CCl_4, is not acted upon by water): the very pure gas is best prepared by the action of water on silicon chloride, since that produced from sodium chloride and sulphuric acid contains traces of hydrogen sulphide:

$$SiCl_4 + 2H_2O = SiO_2 + 4HCl.$$

The properties of hydrogen chloride.—Hydrogen chloride is a colourless gas with a most irritating acid smell; it does not support the

combustion of a taper. The gas fumes strongly in moist air. It has a higher refractive index than most gases, but those of hydrogen bromide and iodide are still higher: the following values refer to sodium light and S.T.P.

Oxygen - -	1·00028	Hydrogen chloride - -	1·000438
Nitrogen - -	1·00030	,, bromide - -	1·000573
Hydrogen - -	1·00014	,, iodide - -	1·000911

The normal density of the gas is 1·6392 gm per litre. When very strongly heated the gas is slightly dissociated into its elements: $2HCl \rightleftharpoons H_2 + Cl_2$; the thermal dissociation of hydrogen chloride, in percentages, is given below:

$t°$ C	427	727	1537	1727
% - -	$1·1 \times 10^{-5}$	$1·34 \times 10^{-3}$	0·274	0·41

The gas is also decomposed to some extent by radium emanation and by ultraviolet light.

Burning sodium introduced into a jar of the gas burns with a bright yellow flame, producing solid sodium chloride and liberating hydrogen:

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

When hydrochloric acid gas is passed through a U-tube cooled in liquid air, it condenses to a snow-white crystalline solid, which sometimes exhibits pink patches, this melts at $-111·4°$ to a colourless liquid, of density 1·184 at the boiling point, $-85·0°$ 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 51·45°; the critical pressure is 81·55 atm.

Aqueous hydrochloric acid.—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 1·231. It contains about 43 per cent. of HCl; the commercial acid contains about 39 per cent., its density being 1·20.

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

EXPT. 17.—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 by displacement (this takes some time) and fitted with a rubber stopper carrying a tube drawn out inside the flask into a jet The flask is inverted with the tube dipping into water coloured with blue litmus contained in a second large flask, as shown in Fig. 103 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, the atmospheric pressure forces the water in the lower flask in the form of a fountain into the upper flask, and the litmus is turned red by the acid solution formed

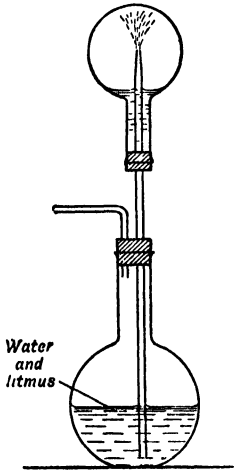


FIG 103 — Demonstration of the solubility of hydrogen chloride

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 distils 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 1 10 very nearly Hence Bineau concluded that the liquid was a chemical compound, $HCl,10H_2O$ The vapour-density was found to be only about 10, showing that the vapour is a mixture of hydrogen chloride and steam. Roscoe and Dittmar (1860), carried out the distillation under various pressures, and found that the concentration of the acid of maximum boiling point decreased with rise of 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	18·7

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 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. By passing hydrogen chloride gas

into the concentrated aqueous acid at −23°, Pierre and Pouchot obtained a crystalline hydrate, $HCl,2H_2O$ (m pt −18°), decomposing on warming Rupert (1907) obtained the hydrate HCl,H_2O.

The composition of hydrogen chloride.—Hydrogen chloride solution is decomposed by electrolysis into hydrogen and chlorine.

EXPT 18.—Electrolyse hydrochloric acid of specific gravity 1·1 in the apparatus shown in Fig 104, 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, nearly 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.

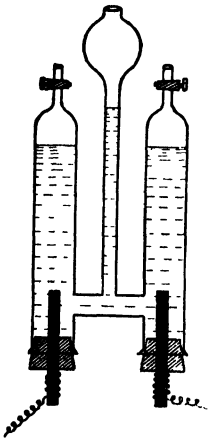


FIG 104.—Electrolysis of hydrochloric acid

Hydrogen chloride gas is decomposed in contact with sodium amalgam, solid sodium chloride is formed and half the volume of hydrogen remains.

EXPT. 19.—Fill the closed limb of the U-tube shown in Fig 105 with dry hydrogen chloride to the lower stopcock, by admitting the gas through the upper stopcock, and running out *dry* mercury from the tube Close the lower stopcock, pour out the mercury, and replace it with liquid sodium amalgam Open the stopcock, so as to bring the gas in contact 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

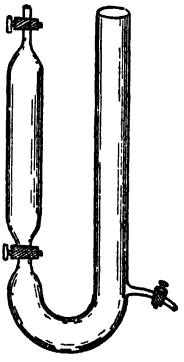


FIG 105.—Decomposition of hydrogen chloride by sodium amalgam

The composition of hydrogen chloride may also be demonstrated by the synthesis of the gas from hydrogen and chlorine.

EXPT. 20.—Fill one half of a strong glass tube, provided with three stopcocks, as shown in Fig. 106, 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 In a room with diffused daylight, open the middle stopcock, and allow the gases to mix After 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 contains hydrochloric acid.

FIG. 106 —Tube for combination of hydrogen and chlorine

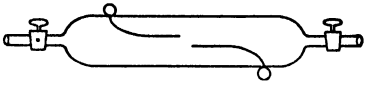


FIG 107 —Explosion tube for hydrogen and chlorine

EXPT 21 —Pass the mixture of hydrogen and chlorine evolved by the electrolysis of hydrochloric acid of specific gravity 1 1 (Fig 109) through a strong glass tube fitted with two stopcocks and platinum firing wires (Fig 107) 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 The tube may be kept wrapped in black paper for a few hours until required Support the tube in a clamp behind a strong glass screen in a dimly-lighted room, and fire 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 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 practically completely

These experiments prove that 1 *volume of hydrogen combines with* 1 *volume of chlorine to produce* 2 *volumes of hydrogen chloride.*

The relative density of the gas (O = 16) is approximately 18·25, hence the molecular weight is approximately 36·5. Since *two* molecules of hydrogen chloride are formed from one molecule of chlorine and one molecule of hydrogen, as the experiments show, the molecular formula is $\frac{1}{2}H_2Cl_2 = HCl$, and this is in agreement with the density.

The atomic weight of chlorine.—By a careful determination of the limiting density of hydrogen chloride, Gray and Burt (1909) found the molecular weight to be 36·187 (H = 1). Hence, the atomic weight of chlorine (H = 1) is 36·187 − 1 = 35·187 or 35·458 (O = 16). 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 bulb containing palladium, 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. 108), the gases being ignited by a spark. The hydrogen chloride was absorbed in water in the bulb Edgar (1908) omitted the water (which gave a little oxygen when chlorine was used in excess), used a quartz apparatus, and condensed and weighed the dry hydrogen chloride in a nickel-plated steel bomb placed in liquid air. The hydrogen, chlorine, and hydrogen chloride were all weighed

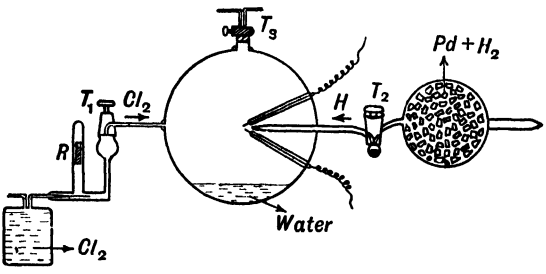


FIG 108.—Atomic weight of chlorine by direct union of chlorine and hydrogen

Photochemical union of hydrogen and chlorine.—A mixture of practically equal volumes of hydrogen and chlorine, containing a trace of oxygen, is obtained by the electrolysis of hydrochloric acid (sp gr. 1·1). The washed gas is passed through a series of *very thin* glass bulbs (Fig. 109), the whole operation being performed in a dark room lighted by a ruby lamp. After the gas has passed for at least half an hour, the two ends of the bulbs are closed with wax, and the *capillaries* separating them *carefully* sealed off with a small flame. The combustion does not usually spread from the heated part. The bulbs are preserved in a dark box.

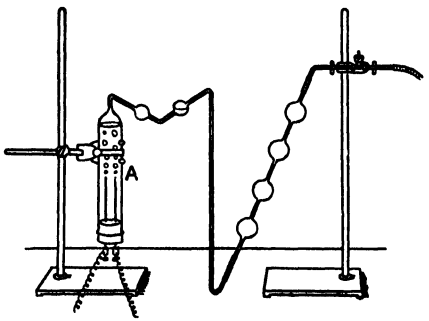


FIG 109 —Filling glass bulbs with a mixture of chlorine and hydrogen.

According to Faraday (1833) concentrated hydrochloric acid, diluted with nine to fifteen parts of water, gives " only a little oxygen with much chlorine at the anode," but experiments by Bunsen showed that the evolution of oxygen begins to be recognisable with 23 per cent acid ; with stronger acids the chlorine is practically pure With more dilute acids, chloric acid is also formed at the anode as well as oxygen The amount of oxygen liberated with 0·1*N* acid is very appreciable, according to Haber and Grinberg (1898)

EXPT 22.—If a bulb containing a mixture of hydrogen and chlorine, protected by a screen of plate glass (Fig 110), is exposed to the light of burning magnesium flash-powder, a sharp explosion occurs, and the glass is shattered. A similar bulb filled with gas dried by passing over P_2O_5 does not usually explode but the gases combine.

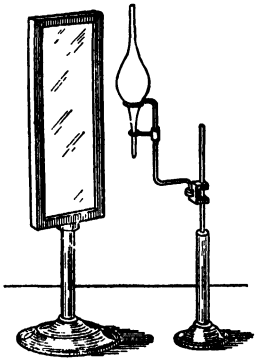


FIG 110.—Explosion of a mixture of hydrogen and chlorine by exposure to strong light of burning magnesium

Heat is evolved in the reaction, hence the action of light consists only in initiating the reaction, which when once started goes on spontaneously. Photochemical reactions which involve an absorption of energy, and which stop when the light is cut off, are the formation of ozone from oxygen, and the decomposition of hydrogen chloride and ammonia, by ultraviolet light.

According to Thos. Thomson, the explosion of a mixture of hydrogen and chlorine on exposure to sunlight was discovered by Dalton, who communicated it to him by letter before the announcement of the experiments of Gay-Lussac and Thenard in 1809.

Pringsheim in 1887 found that if the mixed gas was dried with phosphorus pentoxide before passing into the bulb, and the latter exposed to magnesium light, there was no explosion, but the bulb became hot and the gases combined completely. Following experiments of H. B. Baker (1894), Coehn and Tramm (1923) found that a carefully purified and dried mixture of hydrogen and chlorine underwent no change on exposure to visible light ($\lambda > 4000$ A U.); a partial pressure of water vapour of 10^{-6} mm. was sufficient to initiate the reaction. With (ultraviolet) light of wave-length smaller than 3000 A.U., however, reaction occurred even with very dry gases. We may perhaps compare this behaviour with the ignition of very dry carbon monoxide-oxygen mixtures by very powerful electric sparks, the same mixtures not being ignited by weak sparks. In some photochemical reactions (*e.g.*, the decomposition of hydrogen iodide), the presence of moisture seems to have no influence. Dixon and Harker (1890) found that the velocity of the detonation wave 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.

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 (1857–59) used the apparatus shown in Fig. 111, 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.

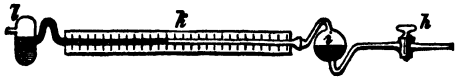


FIG 111 —Actinometer of Bunsen and Roscoe

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 retard the velocity of combination but do not give rise to a period of induction.

The law of photochemical equivalence.—Planck, in 1900, assumed that the energy of light and radiation in general may be absorbed and emitted in definite **quanta**, the quantum, ϵ, for each wave-length, or frequency ν, ($\nu = c/\lambda$, where c = velocity of light; λ = wave-length) being equal to the product of ν and a universal constant, h, called **Planck's constant**: $h = 6{\cdot}55 \times 10^{-27}$ erg seconds, *i e*,

$$\epsilon = h\nu \quad \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

In the case of the yellow light emitted from a sodium flame, for example, $\nu = 5{\cdot}01 \times 10^{14}$, $\therefore \epsilon = 6{\cdot}55 \times 10^{-27} \times 5{\cdot}01 \times 10^{14} = 3{\cdot}28 \times 10^{-12}$ ergs The smaller the wave-length, the larger is the energy of the quantum, and it is found that, in general, light of short wave-length (blue, violet or ultraviolet) is chemically more active than light of longer wave-length (yellow or red). There is reason to believe that a single quantum of light of wave-length 5400 A U can be detected by a normal eye fully adapted in darkness (Noddack, 1924)

Einstein in 1912 assumed that the **primary process** in a photochemical change is the absorption of one quantum of energy from the radiation by each reacting molecule, so that the energy absorbed per mol is (N_0 = Avogadro's constant, $6{\cdot}06 \times 10^{23}$, p 225):

$$E = N_0 h\nu. \quad \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

This primary process is often succeeded by further changes, which occur spontaneously with evolution of energy, so that the yield may exceed, sometimes considerably, that calculated by the **law of photochemical**

equivalence, (2), which is in some senses analogous to Faraday's law of electrochemical equivalence (p 241)

$$Q = \mathbf{N}_0 en,$$

where Q is the quantity of electricity required to set free one mol ($\mathbf{N}_0$ molecules) of an ion of charge ne, n being the valency and e the charge on the electron

In the decomposition of hydrogen bromide by light, for example, Warburg (1916) found that 2HBr are decomposed per quantum This may be explained by the assumption of a primary quantum reaction

$$(1)\quad HBr + h\nu = H + Br,$$

followed by two exothermic spontaneous reactions (which will occur in the dark),

$$(2)\quad H + Br_2 = HBr + Br,$$
$$(3)\quad Br + Br = Br_2$$

It may also be explained by the formation of an **activated molecule** (*i e*, one with more than the average energy corresponding with the temperature) by a primary process.

$$(1)\quad HBr + h\nu = HBr',$$

followed by a collision of this with another HBr molecule

$$(2)\quad HBr + HBr' = H_2 + Br_2$$

The products of the primary reaction may also undergo a cycle of changes so as to be reproduced, in which case the quantum efficiency would be infinite unless the " chain reaction " is broken at some link by collision with a foreign molecule (*e g*, oxygen) In the union of hydrogen and chlorine, at least a million molecules of hydrogen chloride can be produced per quantum Nernst suggests the following mechanism

I Primary (quantum) reaction $Cl_2 + h\nu = 2Cl$ (absorbs energy)

II. Secondary reactions (exothermic)

$$\left.\begin{array}{l} \rightarrow Cl + H_2 = HCl + H, \\ H + Cl_2 = HCl + Cl \rightarrow \end{array}\right.$$

Taylor and Marshall (1923) found that when atomic hydrogen is added to a mixture of hydrogen and chlorine, more hydrogen chloride than corresponds with its amount is formed

In some reactions **photosensitisation** occurs Phosgene, $COCl_2$, is a colourless gas absorbing only in the region of the ultraviolet and therefore, according to the **Grotthuss-Draper law** (1818, 1841) that only rays which are absorbed are effective in producing chemical change, is not decomposed by visible light If chlorine, which absorbs blue light, is mixed with phosgene and the mixture exposed to ordinary light, the phosgene is decomposed by the energy absorbed by the chlorine, which acts as a **photochemical sensitiser**: $COCl_2 = CO + Cl_2$. The combination of hydrogen or sulphur dioxide with oxygen is also sensitised by chlorine

The chlorine industry.—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 a copper salt, which acts as a catalyst, so as to produce chlorine (**Deacon process**): $4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$. The gas may also be dissolved in water, and the solution (*spirit of salt*) decomposed by heating with manganese dioxide (**Weldon process**): $4HCl + MnO_2 = 2H_2O + MnCl_2 + Cl_2$. Large quantities of chlorine are now prepared directly from common salt by electrolysis (p. 204).

The first step in the manufacture of alkali by the Leblanc process (p 757) 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, which proceeds at moderate temperatures, giving mainly acid sodium sulphate, $NaHSO_4$, the second is carried out by heating the resulting mixture of acid sulphate and common salt at a dull red heat, when the normal sulphate, Na_2SO_4, is produced.

$$2NaCl + H_2SO_4 = NaHSO_4 + NaCl + HCl = Na_2SO_4 + 2HCl.$$

Half a ton of coarse-grain salt is charged into the large hemispherical cast-iron saltcake pan, *A* (Fig 112), 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 complete, the pasty mass is raked into the closed fire-brick box, or *muffle*, *B*, heated externally by flames from the fireplace, *C*, which functions as a gas producer. The hydrochloric acid gas passes out through the pipe *d*. Saltcake is left in the muffle.

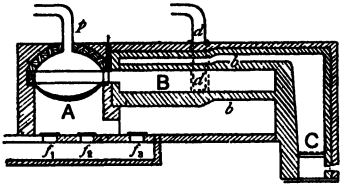


FIG 112.—Saltcake muffle furnace

In the **Hargreave's process**, hot gases from pyrites burners, consisting of sulphur dioxide, oxygen and nitrogen, are passed together with steam over porous pieces of common salt in large iron cylinders. Sodium sulphate is slowly formed, and hydrochloric acid gas evolved:

$$4NaCl + 2SO_2 + 2H_2O + O_2 = 2Na_2SO_4 + 4HCl.$$

The gas from the saltcake furnaces is cooled by passing through 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 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. 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 Weldon process.—Chlorine was formerly made for producing bleaching liquor, from salt, manganese dioxide and sulphuric acid in stoneware jars heated in a water-bath. In 1836 Gossage began to condense the hydrochloric acid evolved in the decomposition of salt with sulphuric acid, in absorption towers. 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, with a grid *A* on which lumps of pyrolusite rest (Fig 113) Hydrochloric acid is run in through the pipe *B*,

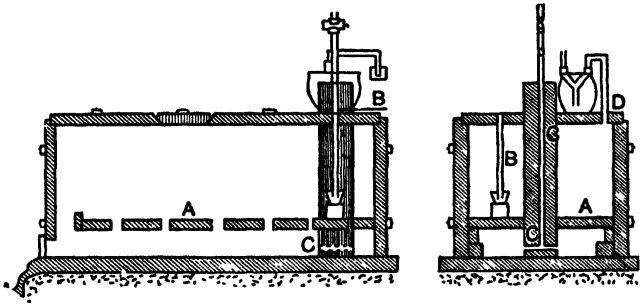


FIG 113 —Chlorine still.

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 undecomposed hydrochloric acid.

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, he hoped to convert it into manganese dioxide, which could be used again: $2Mn(OH)_2 + O_2 = 2MnO_2 + 2H_2O$. The precipitation and oxidation were incomplete; Volhard showed that this was partly due to the acidic character of manganese dioxide, which combined with the basic manganous oxide 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, 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 precipitated and is largely oxidised to the dioxide, the latter combining with the lime, a stronger base than MnO

The acid liquor from the stills is neutralised with limestone and the ferric hydroxide precipitated is allowed to settle out The liquor is then pumped into an **oxidiser**, consisting of a large cylindrical iron tank, where it is treated with the requisite excess of milk of lime, is heated to 60° by steam, and a powerful blast of air is then forced through it 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 is then run into settling-tanks, where a thin black mud, called **Weldon mud,** settles out The clear liquor containing calcium chloride is drawn off; the mud (calcium manganite) runs down into chlorine stills, where it is treated with hydrochloric acid and steam, producing chlorine and manganese liquor The latter goes through the Weldon process repeatedly, but fresh manganese dioxide must be added to replace losses The complete reaction in the Weldon process has been given as follows

$$124MnCl_2 + 160CaO + 49O_2 = 36(CaO,2MnO_2) + 26(MnO,MnO_2) + 124CaCl_2$$

The Deacon process.—The oxidation of hydrochloric acid gas by atmospheric oxygen in the presence of cupric chloride as a catalyst was applied by H Deacon and F. Hurter in 1868 as a technical process for the preparation of chlorine:

$$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2.$$

Hasenclever in 1883 improved the method, and chiefly in his hands the process became a successful technical operation, which almost completely displaced the older and wasteful Weldon process.

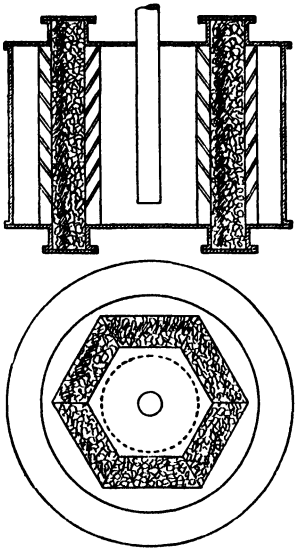


FIG. 114.—Deacon converter.

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 used 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. 114). He dissolved the crude gas from the saltcake furnaces in water in a tower, and ran the aqueous acid in a slow stream into concentrated sulphuric acid, blowing out the hydrochloric acid gas with a current of air. The mixture of 4 vols. of

air and 1 vol. of hydrochloric acid gas 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 decomposer, which is kept at this temperature by hot flue gases from the preheater. About two-thirds of the HCl is decomposed, and the rest is washed out of the gas with water in a coke-tower. The gas, containing 5–10 per cent. of chlorine, diluted with nitrogen, is then dried in a sulphuric acid tower and used in making bleaching powder.

The Deacon reaction is reversible, and the decomposition of HCl diminishes with rise of temperature Below 350°, however, there is practically no decomposition, and the reaction becomes sufficiently rapid only at 425°–450°. There are 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 The Deacon process, which displaced the Weldon method, has now been rendered almost obsolete by the electrolytic processes

Electrolytic chlorine and alkali.—The electrolysis of brine, *i.e.*, a solution of sodium chloride, is applied on a large scale for the production of caustic soda and chlorine. The salt in solution is decomposed by an electric current, chlorine being evolved from the positive pole (*anode*) and a solution of caustic soda and hydrogen gas being formed at the negative pole (*cathode*):

$$2NaCl + 2H_2O = Cl_2 + \underbrace{2NaOH + H_2}_{\text{cathode}}.$$
anode

The reaction may be considered as taking place in two stages, in the first of which sodium is deposited at the cathode and chlorine at the anode; the sodium then reacts with the water, forming a solution of caustic soda and evolving hydrogen:

$$2NaCl = 2Na + Cl_2;$$
$$2Na + 2H_2O = 2NaOH + H_2.$$

Various types of electrolytic cells are used in the process.

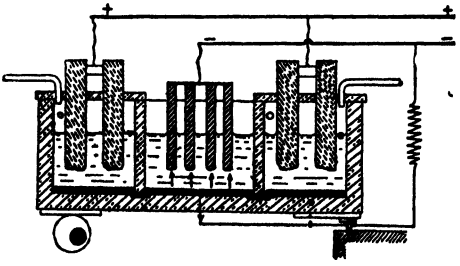


FIG. 115 —Castner-Kellner Cell.

The **Castner-Kellner cell** consisted (Fig 115) 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 are placed in the end compartments, whilst the cathode consists of mercury and a bundle of iron rods in the central compartment Ninety per cent. of the current passes from the mercury in the middle compartment to the iron cathode, and ten per cent through a resistance in parallel Chlorine is evolved in the end compartments, and is led off by earthenware pipes. Sodium discharged on the mercury in the end compartments, acting as a cathode, dissolves, forming sodium amalgam The cell is given a slow rocking motion by an eccentric, and the amalgam is brought from the end compartments to the middle compartment, where it acts as an anode and 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

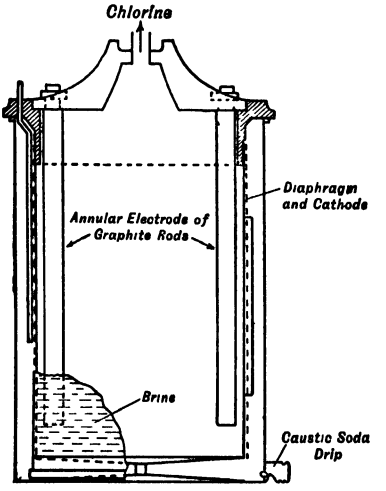


FIG 116 —The Gibbs cell.

In the **Gibbs cell** (Fig 116), used by the United Alkali Co at Widnes, the anodes are carbon rods separated from the cylindrical iron cathode by a diaphragm of asbestos paper The solution of caustic soda then obtained is not so pure as that obtained in the Castner-Kellner cell, and the sodium chloride contained in it must be separated by crystallisation

Chlorine is 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 tanks or cylinders. The electrolytic chlorine is purer than that made by chemical methods. Some of it is used in making stannic chloride, or chlorinated acetylenes. Pure hydrochloric acid is prepared by combining electrolytic hydrogen and chlorine by combustion, and absorption in water. Chlorine is also used in the preparation of bleaching powder and of hypochlorite solutions for bleaching and for petroleum refining.

CHAPTER XIV

VALENCY

Valency.—Hydrogen compounds contain one atom of an element 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, contains 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.* Chlorine, oxygen, nitrogen, and carbon are **uni-**, **bi-**, **ter-**. and **quadri-valent** respectively

Univalent chlorine may be used instead of hydrogen in determining valencies, which when so found are the same as those referred to hydrogen, but **quinque-** 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 chlorine monoxide, Cl_2O, and calcium chloride, $CaCl_2$, oxygen and calcium are bivalent. When calcium and oxygen combine, we should therefore 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, quicklime, has the formula CaO. Calcium can also *displace* two atoms of hydrogen from hydrogen chloride: $2HCl + Ca = CaCl_2 + H_2$. 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 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. 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 :

$$\text{Atomic weight} = \text{Equivalent} \times \text{Valency}$$
$$\text{or} \quad \text{Valency} = \text{Atomic weight/Equivalent}$$

Historical.—E Frankland (1852) by examining series of formulae such as those given above found that " no matter what the characters of the uniting atoms may be, the combining power of the attracting element . . is always satisfied by the same number of these atoms," and that the formula of a compound depends on this Kekulé in 1858 showed that carbon atoms in organic compounds are quadrivalent and are able to combine with one another to form chains Van't Hoff and Le Bel in 1874 showed that, if the four valencies of a carbon atom point in space towards the corners of a regular tetrahedron, this would explain optical activity Werner from 1893 onwards extended the theory of the structure of inorganic compounds, and the electrical theory of the atom has given a satisfactory picture of the nature of valency

Oxygen compounds.—If we examine a series of oxygen compounds : Na_2O (Ca_2O_2) Al_2O_3 (C_2O_4) P_2O_5 (S_2O_6) Cl_2O_7 (Os_2O_8) we see that two additional higher valencies, 7 and 8, appear Chlorine is **septavalent** and osmium **octovalent**, in their highest oxides. (The formulae 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 may classify all the elements in nine groups, according to their valencies The same element may fall into several groups, since the valency is not a constant for an element but may vary according to the nature of the other element with which it is combined, *e.g.*, 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

I. **Univalent elements** : hydrogen, halogens, nitrogen in nitrous oxide, N_2O, alkali-metals, silver, mercury in mercurous compounds (HgCl, Hg_2O), copper in cuprous compounds (CuCl, Cu_2O), gold in AuCl and Au_2O

II **Bivalent elements** : oxygen, nitrogen in nitric oxide, NO, sulphur in H_2S, 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), platinum in platinous compounds A large number of elements are bivalent

III **Tervalent elements** : boron, nitrogen in NH_3 and NCl_3, phosphorus in PH_3 and PCl_3, arsenic in AsH_3, $AsCl_3$, As_2O_3, aluminium, iron in ferric compounds ($FeCl_3$, Fe_2O_3), antimony, bismuth, gold in $AuCl_3$

IV **Quadrivalent elements** : carbon, chlorine in ClO_2, silicon, nitrogen in nitrogen dioxide, NO_2, sulphur in SO_2, lead in plumbic compounds ($PbCl_4$, PbO_2), tin in stannic compounds ($SnCl_4$, SnO_2), platinum in platinic compounds

V. **Quinquevalent elements** : phosphorus, arsenic, and antimony in higher halogen or oxygen compounds (PCl_5, As_2O_5, $SbCl_5$), chlorine in chloric acid, $HClO_3$, and chlorates

VI. **Sexivalent elements** : sulphur in SF_6 and SO_3, tungsten in WCl_6, manganese in manganese trioxide, MnO_3, and manganates, K_2MnO_4

VII **Septavalent elements** : chlorine in Cl_2O_7, iodine in periodates, KIO_4, manganese in Mn_2O_7 and permanganates, $KMnO_4$

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)
PCl_5 (5)	SO_3 (6)

or in its compounds with *different* elements ·

PH_3 (3)	SH_2 (2)
P_2O_5 (5)	SF_6 (6)

It will be noticed that the valency is usually either odd or even, but exceptions are known, *e.g* , WCl_5 (5), WCl_6 (6), and NH_3 (3), NO (2) ; HCl (1), ClO_2 (4).

The lowest valency is always shown in the hydrogen compounds, and the highest valency in the oxygen compounds. The sum of the hydrogen valency and the maximum oxygen valency is often equal to 8. This is **Abegg** and **Bodländer's rule** (1899).

SiH_4 (4)	PH_3 (3)	SH_2 (2)	ClH (1)
SiO_2 (4)	P_2O_5 (5)	SO_3 (6)	Cl_2O_7 (7)

If an element, especially a metal, forms two or more series of compounds in which it has different valencies, the properties of the com-

pounds in these series are usually different. As an example, compare the properties of ferrous (bivalent iron) and ferric (tervalent iron) compounds:

Ferrous sulphate.	Ferric sulphate.
1. Green crystals, $FeSO_4,7H_2O$	1 Colourless crystals $Fe_2(SO_4)_3$, $9H_2O$
2. White precipitate $Fe(OH)_2$ with alkali.	2 Brown precipitate $Fe(OH)_3$ with alkali
3 White precipitate with potassium ferrocyanide	3 Dark-blue precipitate with potassium ferrocyanide
4 Dark 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, these tests would lead us to conclude that we had to do with salts of two different elements.

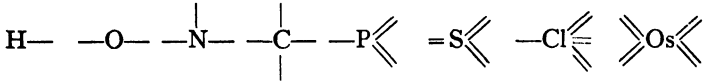
Compounds of an element in which it has a particular valency may resemble compounds of another element with the same valency more closely than they resemble other compounds of the first element with a different valency. Thus, silver, mercurous, and cuprous chlorides are all white, sparingly soluble solids: AgCl, HgCl, CuCl. Mercuric and cupric chlorides, $HgCl_2$ and $CuCl_2$, are soluble; the latter is yellow when anhydrous. 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 ,, ,,

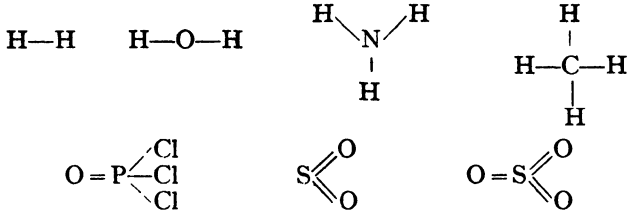
In order to distinguish between the various valencies of an element, a Roman numeral representing the valency may be written over the symbol. Thus, $H_2\overset{VI}{S}O_4$ indicates that sulphur in sulphuric acid is sexivalent:

I	II	III	IV	V	VI	VII	VIII
H	O	N	C	P	S	Cl	Os.

Structural formulae.—We may represent the combination of atoms by drawing from the symbol of an element as many straight lines as it has valencies .

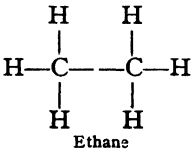


and then making up the formulae of compounds so that no free valencies are left over, each pair of associated lines being written as one :

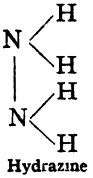


These lines, which for the present have a formal significance, and in particular must not be understood to signify " forces," are called **bonds**, since they represent, as it were, the manner in which the atoms in a compound are *linked* together.

Multivalent atoms can link with each other, by utilising one or more bonds on each atom, the remaining bonds being free to attach other atoms :

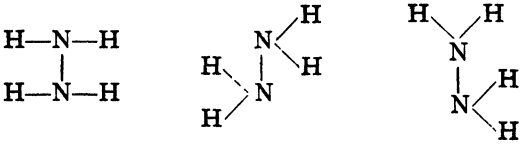


Ethane



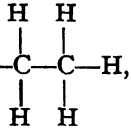
Hydrazine

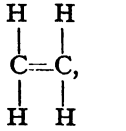
Such formulae are called **structural formulae** ; they represent the way in which the atoms are united, but not necessarily their actual positions, in the molecules. Thus, the formula for hydrazine shows that two nitrogen atoms are united by a bond, and each nitrogen atom is directly united with two hydrogen atoms, in each case by a bond. But all the following formulae, which would correspond with different positions in the molecule :



express exactly the same thing, and are therefore really identical.

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,  **single bond**, or linkage, between carbon atoms.

2. Ethylene,  **double bond**, or linkage, between carbon atoms.

3. Acetylene, H—C≡C—H, **triple bond**, or linkage, between carbon atoms.

Such double and triple bonds are often represented by dots, to save space in printing, thus . $H_3C{\cdot}CH_3$, $H_2C\ CH_2$, HC CH, or usually, $CH_3{\cdot}CH_3$, $CH_2{:}CH_2$, $CH \cdot CH$.*

The propriety of this representation is shown by the fact that molecules with multiple bonds are **unsaturated** ; they can add on other atoms to form **saturated** compounds :

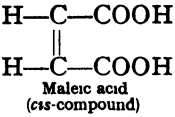
$$CH{:}CH \xrightarrow{+H_2} CH_2{:}CH_2 \xrightarrow{+H_2} CH_3{\cdot}CH_3.$$

The multiple linkages, therefore, contain **latent bonds**, each linkage when broken giving *two* available bonds :

$$HC{\equiv}CH \rightarrow HC{=}CH \xrightarrow{H_2} H_2C{=}CH_2 \rightarrow H_2C{-}CH_2$$

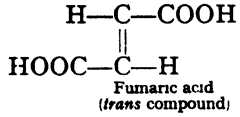
$$H_2C{-}CH_2 \xrightarrow{H_2} H_3C{-}CH_3 \text{ (saturated).}$$

Groups united by a double (or triple) bond are supposed to be restrained from free rotation, whilst those united by a single bond are supposed, in most cases, to be capable of rotation. Thus, although all the formulae of hydrazine on p. 210 are identical, the two compounds :



Maleic acid
(*cis*-compound)

and



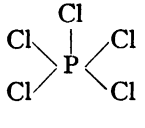
Fumaric acid
(*trans* compound)

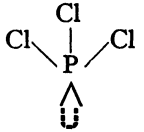
in which the carbon atoms are linked by a double bond, are different isomeric compounds. Isomerism of the type shown by $(H{\cdot}C{\cdot}COOH)_2$ is

* There is some chance of confusion of these with electronic formulae (p. 352).

called **stereoisomerism**, since it is due to the different arrangements of the atoms or groups in *space* (Greek στερεός).

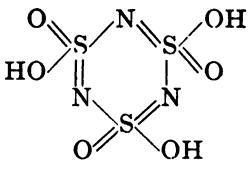
Kekulé assumed that variable valency is always due to latent bonds. Phosphorus was supposed to be always quinquevalent, but in compounds in which it is apparently tervalent two bonds are latent or unsaturated :



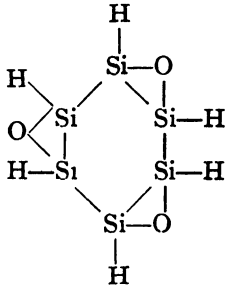


Support was lent to this idea by the circumstance, pointed out by Odling, that when the valency of an element changes, it usually does so *two* units at a time. This, however, is not always the case. The discovery of such compounds as InCl, $InCl_2$, and $InCl_3$ vitiated this hypothesis.

In some cases the atoms in a molecule form closed rings, compounds of this kind, called **cyclic** or **ring compounds**, are more common in the case of certain groups of carbon compounds (organic compounds), but are known also in the case of some other elements



Trisulphimide.



Siloxene.

Ozone

Valency of radicals.—The conception of valency may be applied also to radicals, groups of atoms which take part as a whole in chemical reactions. An inspection of the table :

HNO_3	H_2SO_4	H_3PO_4	Na_3PO_4
$NaNO_3$	K_2SO_4	NaH_2PO_4	$NaNH_4HPO_4$
NH_4NO_3	$(NH_4)_2SO_4$	Na_2HPO_4	$(NH_4)_3PO_4$

leads to the recognition of the following radicals in the compounds :

$$—NO_3, \ =SO_4, \ \equiv PO_4, \text{ and } —NH_4.$$

If we know the valencies of the elements and of common radicals, we can at once write down the formulae of all the compounds which can *theoretically* be formed from them.

It is usually most convenient to remember the formulae 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 formulae $AlCl_3$ 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 $Al_2(SO_4)_3$.

Positive and negative valencies.—Valencies are sometimes classified as positive and negative, the former being the valencies of atoms or radicals attracted to the negative electrode (cathode) in electrolysis, and the latter those attracted to the positive electrode (anode). In this way, we first consider the electrochemical character of the element, apart from its valency. This electrochemical character is epitomised in the table on p. 111; metals and hydrogen are **electropositive** and oxygen and halogens **electronegative**; other elements are sometimes electropositive and sometimes electronegative.

In its compounds with hydrogen or metals an element is assumed to be electronegative (except metals in hydrides, such as Li^+H^-; see p. 777), whilst in its compounds with oxygen, halogens or sulphur it is electropositive. This **polar character** of elements was particularly emphasised in the **electrochemical** or **dualistic theory** of Berzelius (1811) Owing to the fact that carbon is an element without electrochemical individuality, the theory was of little service in the early study of carbon compounds, and since this branch of chemistry monopolised the attention of many chemists in the last century, Berzelius's theory was neglected or considered to be erroneous.

Elements of low valency (halogens; alkali metals) are outstandingly negative or positive; as the hydrogen valency increases, the sharp definition of properties falls off, and in elements of the maximum hydrogen valency of four, especially carbon, it has practically disappeared. For the present, we may call the valency of alkali metals +1, that of halogens in simple compounds −1, that of sulphur in H_2S −2, in H_2SO_4 +6, that of chlorine in Cl_2O_7 +7, and so on, whilst that of carbon we call simply 4. The notation is extended to radicals; the valency of NH_4 is +1, that of SO_4 is −2. The full meaning of this classification of valencies is explained later by the electrical theory of the atom.

Molecular compounds.—Saturated molecules often have the capacity of uniting with each other, although they cannot take up additional *atoms* of elements. Hydrofluoric acid, HF, and potassium fluoride, KF, although both saturated compounds, combine to form the salt

potassium hydrogen fluoride, KHF_2. This is readily broken up on heating into KF and HF, and hence is often formulated as KF,HF, and called a **molecular compound.**

An explanation of the formation of compounds from apparently saturated molecules may be given 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 may be represented by dotted lines instead of by bonds; they are less than a unit of free valency as exhibited by a hydrogen atom : $\overset{+}{K}F\ldots$ and $\overset{-}{H}F\ldots$ 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.

This hypothesis recognises 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 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.

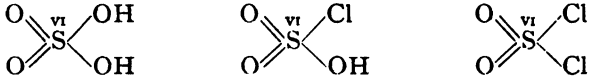
The molecular weight of a substance can be found from vapour density and also in solution. Hence the compound must be volatile, or must dissolve without decomposition in a solvent, in order that its molecular weight, and the valency of a constituent element, can be found The presence of certain **groupings of atoms** in a compound may often be inferred from chemical reactions, and this may lead to the structural formula of the compound.

Sulphuric acid, H_2SO_4, for example, when treated with phosphorus pentachloride, forms the two compounds $HClSO_3$ and SO_2Cl_2 in succession.

$$H_2SO_4 + PCl_5 = HClSO_3 + POCl_3 + HCl,$$
$$HClSO_3 + PCl_5 = SO_2Cl_2 + POCl_3 + HCl.$$

In each of these reactions the hydroxyl radical, OH, is replaced in the acid by an atom of chlorine, so that the formula of sulphuric acid may be written $SO_2(OH)_2$, and that of the compound $HClSO_3$ as $SO_2(OH)Cl$. The sulphuryl radical SO_2 (which is not the same as the sulphur dioxide *molecule*) must, therefore, be bivalent, since OH and Cl are univalent. If we assume that the sulphur atom has its maximum valency of six,

as in SF_6, the structures of sulphuric acid and of the two other compounds may be represented by the formulae (see, however, p 519)



The following formulae have been found from direct measurements of vapour densities, in some cases (*e g*, AgCl at 1735°) at very high temperatures

NaCl	$BeCl_2$	$AlCl_3$ (above 800°)	$TiCl_4$	$NbCl_5$	WCl_6
KCl	$CrCl_2$	$CrCl_3$	VCl_4	$TaCl_5$	
KI	$FeCl_2$	$FeCl_3$ (at 750°)	$GeCl_4$	$MoCl_5$	
RbCl	Cu_2Cl_2	$GaCl_3$	$SnCl_4$	WCl_5	
	Hg_2Cl_2				
CsCl	$ZnCl_2$	$InCl_3$	$ZrCl_4$		
CsI	$GaCl_2$	$SbCl_3$	UCl_4		
AgCl	$SnCl_2$	$BiCl_3$			
InCl	$InCl_2$				
TlCl	$HgCl_2$				
	$PbCl_2$				

In a few cases the valency has been confirmed by the vapour densities of volatile **organo-metallic compounds**: zinc methyl $\overset{II}{Zn}(CH_3)_2$, lead tetraethyl $\overset{IV}{Pb}(C_2H_5)_4$, aluminium acetylacetonate $\overset{III}{Al}(C_5H_7O_2)_3$, and tin triethyl $\overset{IV}{Sn}_2(C_2H_5)_6$.

The valency of an element may be determined from the ratio of the atomic weight to the equivalent. According to Dulong and Petit's law, 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 known. In some cases the equivalent may be determined by making use of Faraday's law of electrolysis (p. 242).

The equivalent of zinc, determined by the amount of hydrogen evolved by the action of zinc on dilute acid, is 32·5 The specific heat of zinc is 0·0955, hence the atomic weight 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 formulae 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. Phosphorus pentachloride, PCl_5, containing quinquevalent phosphorus, is decomposed by **heat** into chlorine and phosphorus trichloride, PCl_3, containing tervalent

phosphorus: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Mercurous oxide is decomposed by exposure to **light** into mercuric oxide and metallic mercury: $Hg_2O = Hg + HgO$, and lead monoxide takes up oxygen to form the dioxide: $2PbO + O_2 = 2PbO_2$. Phosphine, PH_3, and hydrogen chloride, HCl, do not combine at ordinary pressure, but under **increased pressure** they give solid phosphonium chloride containing quinquevalent phosphorus: $PH_3 + HCl \rightleftharpoons PH_4Cl$. By **electrolysis**, a solution of manganous sulphate, $\overset{II}{Mn}SO_4$, in sulphuric acid, is converted into permanganic acid, $H\overset{VII}{Mn}O_4$.

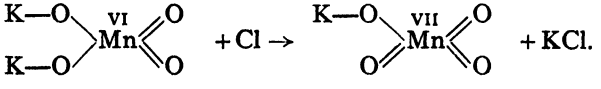
Chemical changes often lead to alteration of valency, according as an excess or deficit of an element or radical is present during the preparation of the compound: $2Hg$ (excess) $+ I_2 = 2HgI$; $Hg + I_2$ (excess) $= HgI_2$ In some cases only one compound is formed under all conditions from the elements, *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 always leads to the formation of stannous chloride: $Sn + 2HCl = SnCl_2 + H_2$

Changes of **oxidation** and **reduction** bring about changes of valency: $\overset{II}{Sn} \rightarrow \overset{IV}{SnO} \rightarrow \overset{IV}{SnO_2}$ (oxidation); $\overset{III}{Fe_2O_3} \rightarrow \overset{II}{FeO}$ (reduction) *Oxidation leads to increase, reduction to decrease, of positive valency* The change of a ferrous to a ferric salt, for example, 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, on the old dualistic theory, 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 positive 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: $\overset{II}{FeCl_2} + Cl \rightarrow \overset{III}{FeCl_3}$. The reverse changes are equivalent to reduction.

An example of oxidation and reduction occurring simultaneously is the action of ferrous sulphate on potassium permanganate.

$$2KMn^{VII}O_4 + 10Fe^{II}SO_4 + 8H_2SO_4 = K_2SO_4 + 2Mn^{II}SO_4 + 5Fe^{III}_2(SO_4)_3 + 8H_2O$$

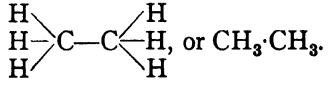
$10Fe^{II}$ becomes $10Fe^{III}$, an *increase* of 10 units of positive valency (**oxidation**).

$2Mn^{VII}$ becomes $2Mn^{II}$, 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 or its equivalent, which can combine with, or be displaced by, one atom of the element Hydrogen valencies vary from 1 to 4. Oxygen is bivalent (H_2O), elements in oxygen compounds can have valencies from 1 to 8 OsF_8 is also known The inactive gases, since they form no compounds, may be regarded as zero-valent

Structural formulae 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 **triple bonds,** which can add on univalent atoms in pairs to form saturated compounds. $CH_2\,CH_2 + Cl_2 = CH_2Cl\,CH_2Cl$.

CHAPTER XV

THE KINETIC THEORY

The kinetic theory of gases.—Dalton in 1801 filled two bottles (Fig. 117), 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 uniformly mixed, as may be shown by opening each under caustic soda solution and measuring the absorption. This spontaneous mixing of gases in opposition to the force of gravity is called **diffusion**, and must be due to the *motion of the molecules* of the gases amongst each other. This motion is not perceptible to the eye because the molecules are very minute.

FIG. 117.—Dalton's experiment on gaseous diffusion.

Similar diffusive motions occur 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. 118), the salt dissolves, and a layer of blue solution is formed. If the jar is set aside in a room of uniform temperature, to avoid convection currents, the blue colour slowly rises through the jar until, after several months, the colour of the solution has become uniform.

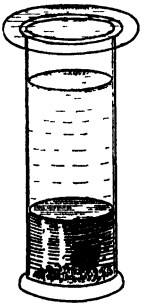


FIG. 118 — Liquid diffusion.

We therefore 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 picture of the condition of a molecular swarm, as conceived to exist in gases and liquids, is called the **kinetic theory** (Greek *kinesis*, motion).

From the slowness of diffusive motion it might seem that the molecular speeds must be small. This is not correct; the molecules in air,

for example, move 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 from one copper vessel into a second exhausted copper vessel, in such a way that it does no external work, it does not become appreciably warmed or cooled He concluded that no appreciable work is done by, or against, forces of repulsion or attraction between the molecules, and hence that *the molecules of gases exert practically no forces on one another.*

The pressure exerted by the gas uniformly over the walls of the containing vessel must, therefore, be wholly kinetic in origin—it must be caused by **molecular bombardment.** On all parts of the surface there is a ceaseless hail of elastic molecules, which impinge on the surface and fly off again into the gas. Without going into detail one can see that this molecular bombardment, distributed over the surface, must appear to our coarse senses as a uniform pressure.

The molecules strike the wall at all angles, from a full normal blow to a glancing impact, and 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. The 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.

One 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 molecules may have all possible speeds from zero to infinity, but Clerk Maxwell (1859) showed that the speeds of the majority of molecules in a gas at a given temperature differ only slightly from a **mean speed,** denoted by Ω. The ordinates of the curve in Fig. 119 represent the fractions of the molecules which have speeds represented by the abscissae. It will be seen that molecules very rapidly become scarcer which have speeds deviating appreciably from the mean speed. If we follow *any* molecule along its zigzag path, we shall therefore find

that they *all* describe these with an almost constant speed, Ω. The *component* velocities, of course, fluctuate repeatedly as the molecules undergo collisions, but the speed along the path of motion is nearly uniform the whole time.

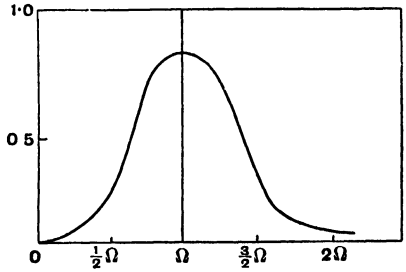


FIG 119 —Distribution of molecular speeds in a gas.

Calculation of the pressure of a gas —Let a mass M of gas be contained in a cube of side L, and let G be the speed of the molecules, assumed provisionally to be the same for all. Let there be N particles in a unit cube. We may suppose that on the average one-third of the particles are moving (in both directions) perpendicular to each pair of faces. The number of impacts per second made by a particle on any one face is $G/2L$, since it traverses a distance $2L$ between each impact with that face. The total number of impacts per second on the face is $G/2L \times (NL^3/3) = NGL^2/6$. The momentum of the molecule, of mass m, before impact is mG; after impact it is $-mG$, hence the change of momentum is $2mG$. The *pressure* per unit area due to all the particles is, therefore: $(NGL^2/6) \times 2mG - L^2$, where L^2 is the area of the face. Thus:

$$p = \tfrac{1}{3}mNG^2.$$

But $mNL^3 = M$, and $L^3 = V$, the volume of the cube, hence, since $M/V = D$ = density of the gas:

$$p = \tfrac{1}{3}DG^2$$
$$\text{or} \quad pV = \tfrac{1}{3}MG^2.$$

The mass of gas striking one cm ^{2} of the wall per second $= \frac{1}{2}mN\bar{u} = \frac{1}{2}D\bar{u}$ where $\bar{u}$ is the mean velocity normal to the wall, in the molecular shower It can be shown, by the usual method of calculating average values in the integral calculus, that if the **mean speed** of the gas molecules is Ω, the average component in any direction is ½Ω, and that $\Omega = 4/\sqrt{6\pi} \cdot G = 0{\cdot}921G$. G is called the **mean square speed,** and is such that the total kinetic energy of translational motion of the molecules is $\frac{1}{2}G^2$ per gm. of gas

Molecular energy.—The **kinetic energy of translation** of a molecule is $\frac{1}{2}mG^2$, hence the equation shows that: *the product of the pressure and volume of a gas is equal to two-thirds of the kinetic energy of translation of the molecules.* The kinetic energy of translation is the energy possessed by the molecules in virtue of their translatory motion in straight lines ; only this part of the energy makes any contribution to the pressure. Energy due to rotation of the molecules, or the relative motions of their parts, is without influence on the pressure

Boyle's law, $pv = \text{const.}$ when the temperature is constant, shows that *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.

Now put $V = 22{\cdot}415$ litres, then at S T P, $M = \mathbf{M}$, the gram-molecule (mol) of the gas, and $N = \mathbf{N}_0$, the number of molecules in a gram-molecule. Avogadro's hypothesis shows that $\mathbf{N}_0$ is the same for all gases; it is called **Avogadro's constant.** We see that *the kinetic energy of translation of the molecules is the same for a mol of any gas at a given temperature* For kinetic energy $= \frac{1}{2}MG^2 = \frac{2}{3}pv$. But v is the same for a 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, $V = 22\ 415$ litres $= 22\ 415 \times 1000\ 028$ cm^3, $p = 760$ mm $= 76 \times 13{\cdot}595 \times 980{\cdot}6 = 1{,}013{,}225$ dynes per cm^2,

$$\therefore \tfrac{1}{2}pV = 22{\cdot}415 \times 1000\ 028 \times 1013225 \times \tfrac{1}{2} = 3{\cdot}407 \times 10^{10} \text{ ergs}$$

Thus, the molecular energy of a mol of any gas at 0°, due to the translatory motion of its molecules, is large enough to raise a weight of about a ton through one foot.

The gas constant is

$$R = pV/T = \tfrac{2}{3} \times 3{\cdot}407 \times 10^{10}/273{\cdot}09,$$
$$\therefore R = 8{\cdot}317 \times 10^7 \text{ ergs/1° C},$$
$$\text{or } R = 8\ 317 \times 10^7/4\ 184 \times 10^7$$
$$= 1\ 988 \text{ g cal /1° C.}$$

Molecular speeds.—From the value of the molecular translational 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 calculate the squares of the molecular speeds, G^2, by division by the molecular weight in grams, $\mathbf{M}$, and multiplication by 2:

$$G^2 = \frac{\frac{1}{2}\mathbf{M}G^2}{\mathbf{M}} \times 2.$$

Thus, for oxygen, $\mathbf{M} = 32$; $\therefore G^2 = 34 \times 10^9 \times 2/32$; $\therefore$ the **mean square speed** G at 0° C. $= 46{,}000$ cm. per sec, or 460 m. per sec. The **mean speed,** Ω, is G multiplied by 0·921, *i.e.*, 425 m. per sec. In the case of hydrogen, the mean speed at 0° is 1694 m. per sec.

MEAN MOLECULAR SPEEDS, Ω, AT 0° IN METRES PER SECOND

(Velocities in the gases are given in brackets)

Hydrogen, 1694 (1286).	Oxygen, 425 (317)
Helium, 1208.	Carbon dioxide, 362 (257).
Steam, 565 (401).	Chlorine, 288 (206)
Nitrogen, 455 (337).	Mercury vapour, 170.

The speed of steam molecules ($\mathbf{M}=18$) is greater than that of oxygen molecules ($\mathbf{M}=32$); the speeds of hydrogen and helium are large relatively to those of the other gases 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 pressure due to the molecular shower is thus explained. It is also seen that the molecular speeds are of the same order as, but greater than, the **velocities of sound**, u, in the gases The formulae $p=\frac{1}{3}DG^2$ and $u=\sqrt{\gamma p/D}$ (p 228), where $\gamma=c_p/c_v$, give $u=\sqrt{\frac{1}{3}\gamma}\ G$

Effusion.—In the phenomenon of effusion, studied by Graham, a gas is forced by pressure through a small aperture in a metal plate exposed to the air. The *relative* rates of effusion of different gases are in the inverse ratio of the square roots of the molecular weights, or densities. 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.**

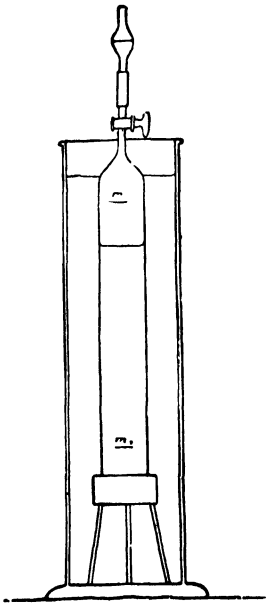


Fig 120 —Bunsen's effusiometer (Ostwald).

Expt. 1 —A glass cylinder has two marks, m_1, m_2, scratched upon it, and is placed in a cylinder of water (Fig 120) 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, t, 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

The amount of work spent in forcing each gas through the aperture, which is represented by the rise of level of the liquid, is the same, hence the kinetic energy imparted to each gas is the same If u_1, u_2 are the velocities of *bulk* motion of the gases, *i e*, the speeds at which the liquid level rises, we shall have

$$\tfrac{1}{2}m_1u_1^2=\tfrac{1}{2}m_2u_2^2,$$

where m_1 and m_2 are the masses of the gases expelled These occupy the same volume, hence $m_1/m_2 = D_1/D_2 = M_1/M_2$, where D is the density and M the molecular weight. Again, $u_1/u_2 = t_2/t_1$, where t is the effusion time. Hence:

$$t_2^2/t_1^2 = D_1/D_2 = M_1/M_2$$

If the effusion is not isothermal, as assumed above, this equation will not apply For adiabatic effusion, the ratio of specific heats $c_p/c_v = \gamma$ is involved.

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 is also 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 on p 221

Thus, the mean speed of hydrogen molecules at 1000° C. is found as follows kinetic energy at 1000° = (1273/273) × $K E$ at 0° C But the speed is proportional to $\sqrt{K E}$;

$$\therefore \text{ speed at } 1000° \quad \text{speed at } 0° = \sqrt{1273} \quad \sqrt{273};$$

$$\therefore \text{ speed at } 1000° = 1700 \times \sqrt{\frac{1273}{273}} = 1700 \times 2\ 16 \text{ m per sec.}$$

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 $\frac{1}{2}MG^2 = \frac{3}{2}pv = \frac{3}{2}RT$. The value of R in absolute units is $8{\cdot}317 \times 10^7$ ergs per 1°, hence the translational kinetic energy at $T°$ absolute is $\frac{3}{2} \times 8{\cdot}317 \times 10^7\ T$ ergs $= 12{\cdot}476 \times 10^7\ T$ ergs. In g. cal. it is $\frac{3}{2} \times 1{\cdot}988\ T = 2{\cdot}982\ T$ g. cal.

The molecular diameter.—In spite of the high values of the molecular speeds the diffusion of one gas into another takes place slowly. Expt. 4 on p. 65 shows that bromine vapour diffuses upwards only very slowly, 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 rate of bulk motion of the bromine vapour is not more than about one hundred thousandth of the molecular speed.

The reason is that the molecules of bromine do not move uninterruptedly in straight lines; they collide with one another and with the air molecules, 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.

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 From the rate of diffusion the **diameters of molecules** may be calculated ; the diameter of the oxygen molecule, assumed spherical, is of the order of 3×10^{-8} cm. $= 3$ A U.

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 6×10^{-7} cm thick, and oil-films on water are only 10^{-7} cm thick, or even less

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: $L = 1{\cdot}25\eta/\sqrt{pD}$. It is greater the lower the pressure, because the molecules are then 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 oxygen molecule at atmospheric pressure is equal to the thickness of the thinnest gold-leaf. At low pressures such as exist in the spaces between the walls of " thermos " flasks, the free path is several cm. A molecule rebounds from opposite walls of such a flask many times without encountering another.

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, is Ω/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.

Shapes of molecules.—The molecular diameter, σ, is calculated in various ways, of which probably the most reliable is from the viscosity of the gas Usually the assumption is made that the molecule is spherical, and although this may be approximately true for diatomic molecules it may not be permissible for rod-shaped molecules, such as carbon dioxide and nitrous oxide (p 585), for which a single "diameter" can have very little meaning More recently, attempts have been made to determine the distances between the atomic centres in such molecules, and these will obviously give a better picture of the structure of the molecule than a fictitious diameter

The following table contains the values of the molecular diameters, σ in A U , on the assumption of spherical molecules, as calculated from the viscosities

He	1·88	H_2	2 39	NO	2 9
Ne	2 36	O_2	2 96	HCl	2 6
A	2 97	N_2	3 13	H_2O	2 6
Kr	3 23	CO	3 22	Cl_2	(1 60) 3 6
Xe	3 54	CO_2	3 39	Br_2	1 71
		N_2O	3 32	I_2	1 88

The distances between the lines in **band spectra** depend on the moments of inertia of the molecules, hence these and from them the distances between the atoms may be calculated In this way and from X-ray measurements it is found that in the gaseous and also in the *solid* state, the molecules of CO_2 and N_2O are rod-shaped, O=C=O, N=O=N. The H_2O molecule is a triangle with O at the apex, the NH_3 molecule is a flat tetrahedron with N at one apex and H at each of the other three Methane is tetrahedral.

Molecular magnitudes.—Important constants in the kinetic theory are : N = the number of molecules per cm.^{3} at S.T.P ; $\mathbf{N}_0 = 22415 \times N$ = the **number of molecules in a gram-molecule.** The number $\mathbf{N}_0$, which is the same for all gases, is called **Avogadro's Constant.** The value of $\mathbf{N}_0$, 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 is due to Rutherford and Geiger. The element radium emits atoms of helium, called **α-rays,** with speeds of about 2×10^9 cm. per sec. (*i e* , about 100,000 times faster than gas molecules), and extremely large kinetic energy. When α-rays from a particle of radium, *A*, impinge on a screen of zinc-blende, *B*, in the **spinthariscope** of Crookes (Fig. 121), each α-particle causes a flash of light visible under a lens, *C*. It was therefore possible to count

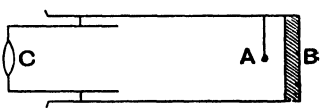


FIG 121 —Spinthariscope

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 mm.^{3} per 24 hours. By comparing this with the 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; its value is $2{\cdot}7 \times 10^{19}$. Thence $\mathbf{N}_0 = 6{\cdot}05 \times 10^{23}$.

A second method used by Rutherford and Geiger (1908) depends on the capacity of the α-particles of rendering a gas through which they pass a conductor of electricity A long glass " firing tube " AA' (450 cm long and 2 5 cm wide), (Fig 122), was exhausted, and at the end A was placed a preparation of radium on a lead plate, a, which expelled

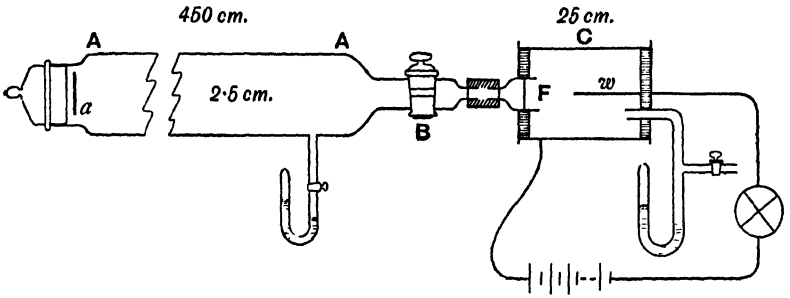


FIG. 122 —Rutherford and Geiger's apparatus

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 ionised. A mica window at F shut off the gas from the evacuated tube, AA' Running axially through 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 were counted, and the method of calculation was similar to that in the first method The value $\mathbf{N}_0 = 6\ 14 \times 10^{23}$ was found

The determinations of $\mathbf{N}_0$ have been made by counting, as above, and from other radioactive experiments, from experiments on colloidal solutions (p. 275), 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.

TABLE OF VALUES OF AVOGADRO'S CONSTANT, $\mathbf{N_0}$

METHOD.	$\mathbf{N_0}$.
Classical kinetic theory - - -	10 $\times 10^{23}$ (approximately)
Cloud formation (p. 11) - -	8 3 $\times 10^{23}$
Brownian movement (p. 274) -	6 30 $\times 10^{23}$
Radiant heat - - - - -	6 19 $\times 10^{23}$
Counting α-particles - - -	6 14 $\times 10^{23}$
Electronic charge (Millikan, p. 244)	6 06 $\times 10^{23}$.

TABLE OF MOLECULAR MAGNITUDES.

Number of molecules per c c of gas at S T P $=N=2\ 70 \times 10^{19}$

Number of molecules per gram-molecule (22·415 litres in ideal state at S T P) $=\mathbf{N_0}=6\ 06 \times 10^{23}$

Mass of hydrogen atom $=0\ 00008\ 9873/(2 \times 2\ 7 \times 10^{19}) = 1\ 67 \times 10^{-24}$ gm

Mean speed of hydrogen molecule at $0° = \Omega_{H2} = 16{\cdot}94 \times 10^4$ cm /sec

Translational kinetic energy of a molecule at $0° = 34{\cdot}1 \times 10^9/6\ 06 \times 10^{23}$ $= 5\ 61 \times 10^{-14}$ erg

Rate of change of translational kinetic energy per 1°

$= 5{\cdot}61 \times 10^{-14}/273\ 09 = 2{\cdot}056 \times 10^{-16}$ erg/degree

A few special magnitudes, not known with the accuracy of the above, may be given for comparative purposes

Diameter of hydrogen molecule $= 2\ 40 \times 10^{-8}$ cm

Mean free path of hydrogen molecules at S T P $= 1{\cdot}22 \times 10^{-5}$ cm

Average distance apart of gas molecules at S T P $= 3 \times 10^{-7}$ cm

Number of collisions per second of oxygen molecules at S T P = $4\ 25 \times 10^9$

Time of describing free path of oxygen molecules at S T P = $2{\cdot}3 \times 10^{-10}$ sec

The specific heats of a gas.—When 1 mol of a gas is heated *at constant volume* from $T°$ to $(T+1)°$ 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 the 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, no heat absorption results from the change of *volume* alone (*cf* p. 219), and the difference of molecular heats, $(C_p - C_v)$, will be equal to the external work done, viz. (*pressure*) × (*increase of volume*);

$$\therefore\ C_p - C_v = p\,(V' - V) = pV\left(\frac{T+1}{T} - 1\right) = \frac{pV}{T} = R.$$

In a **monatomic gas** the heat absorbed increases exclusively the

kinetic energy of translation of the molecules (p. 220), and for 1° rise of temperature this increase of energy will be :

$$\frac{1}{T}\left(\frac{MG^2}{2}\right)=\tfrac{3}{2}R=2\cdot982 \text{ g. cal.}$$

Hence, $C_v=2\cdot982$ g cal. But $C_p=C_v+R=4\cdot970$ g. cal., hence the ratio of specific heats for a monatomic gas is

$$C_p/C_v=c_p/c_v=\gamma=4\cdot970/2\cdot982=1\cdot667.$$

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 total extra energy is denoted by E, per 1° rise of temperature, we shall have .

$$C_p/C_v=\frac{\frac{3}{2}R+R+E}{\frac{3}{2}R+\quad E}<\frac{\frac{3}{2}R+R}{\frac{3}{2}R}<1\cdot667.$$

The value of C_p/C_v for a gas, the molecules of which contain more than one atom, is found to be less than 1·667, as the table below shows.

Gas	For-mula	C_p/C_v at 15°	Gas	For-mula	C_p/C_v at 15°.
Helium	He	1 667	Carbon dioxide	CO_2	1 302
Oxygen	O_2	1·396	Nitrous oxide	N_2O	1 300
Nitrogen	N_2	1 405	Ammonia	NH_3	1 310
Air	$4N_2+O_2$	1 403	Sulphur dioxide	SO_2	1 285
Hydrogen	H_2	1 411	Hydrogen sulphide	H_2S	1·340
Carbon monoxide	CO	1·404	Methane	CH_4	1 310
Hydrogen chloride	HCl	1·400	Ethylene	C_2H_4	1 250
Chlorine	Cl_2	1·355	Steam	H_2O	1·306 (100°)

Even in the case of gases containing the same number of atoms in the molecule (O_2, Cl_2, SO_2, H_2S), γ has different values, the lower values indicate the presence of additional rotations or vibrations in the molecules to which they refer

The value $C_p/C_v=1$ 667 was found for mercury vapour by Kundt and Warburg in 1876, and thus the monatomic character of the mercury molecule, inferred from vapour densities and on chemical grounds, was confirmed. The method was also used by Ramsay in the case of argon, etc , elements which form no chemical compounds and for which no other method was available in the determination of the atomic weight. In this case, also, the molecules were found to be monatomic

The values of γ for a gas is usually determined either by methods depending on the formula for the **velocity of sound** :

$$u=\sqrt{\gamma p/D}=\sqrt{\gamma RT/M} \text{ for an ideal gas,}$$

or methods depending on the formula for the **adiabatic expansion** of the gas :

$$pv^{\gamma}=\text{const}, \quad \text{or} \quad pT^{\frac{\gamma}{\gamma-1}}=\text{const.}$$

Measurements of the specific heats of diatomic gases give values for the moments of inertia of the molecules and thence, since the moment of inertia is of the form Σmr^2, of r, the distance between the atoms

At low temperatures the rotational energy of the hydrogen molecule falls off, and at about $-230°$ C. this part of the energy has become zero The molecular heat then assumes the value $C_v = 2\ 982$ for *monatomic* gas This is explained by the hypothesis that the energy of rotation (and also that of the vibration of the atoms, if this form of energy is present) is regulated by the quantum law (p 385), and decreases with temperature much more rapidly in the regions of low temperatures than the value $\frac{1}{2}RT$, the classical expression for the energy of each degree of freedom of rotation, or RT for each vibration The effect is measurable only with hydrogen

Molecular attraction.—We have so far assumed that the forces exerted on one another by gas molecules are negligibly small This is only approximately true. Gases are usually more compressible than according to Boyle's law, and this may be explained by assuming that the molecules attract one another, the attraction becoming 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. A liquid is much less compressible than a gas, and the compressibility of a gas also falls off considerably at high pressures. This effect is assumed to be due to the space occupied by the molecules, x, if this is comparable with the total space, v, only the intermolecular space $(v - x)$ is available for compression.

These two factors are taken into account by the **equation of Van der Waals**, which replaces the ideal gas equation $pv = RT$ by :

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

where a and b are constants. The term 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 good results with some gases (*e.g.*, ethylene), but the attraction term depends on the temperature, hence D. Berthelot has used the equation :

$$\left(p + \frac{a'}{Tv^2}\right)(v - b) = RT,$$

with remarkably good results at moderate pressures, and it has been given a theoretical foundation by Keesom (1912). The constants in Van der Waals's equation are related to the critical constants (p. 139) as follows :

$$a = 3p_c v_c^2\ ;\quad b = v_c/3\ ;\quad p_c v_c = 3RT_c/8.$$

If we assume that the molecules are spherical and of radius r, we

have $4 \cdot \frac{4}{3}\pi r^3 \mathbf{N}_0 = b$. For carbon dioxide, $b = 42{\cdot}8$ cm.^{3} per mol, hence :

$$r = \sqrt[3]{\frac{42{\cdot}8 \times 3 \times 7}{4 \times 4 \times 22 \times 6{\cdot}06 \times 10^{23}}} = 1{\cdot}615 \times 10^{-8} \text{ cm},$$

or $d = 3{\cdot}23 \times 10^{-8}$ cm., which is smaller than the value ($3{\cdot}39 \times 10^{-8}$ cm) calculated from the viscosity.

Liquids.—The attractive forces exerted by molecules upon one another are of considerable magnitude when the substance is in the liquid state. In a liquid the molecules are close together, so that there are practically no free paths. The motion is now more analogous to gliding of the particles among and over one another.

Since the actual space occupied by spheres of radius r most densely packed is 0·74 of the total volume, then if we assume that in a liquid the molecules are in contact, we find :

$$\frac{4}{3}\pi r^3 \mathbf{N}_0 = 0{\cdot}74\, V,$$

where $\mathbf{N}_0$ is Avogadro's constant and V the molar volume (= Mol. wt /Density) This equation gives an *approximate* value of the molecular radius, r, in a liquid.

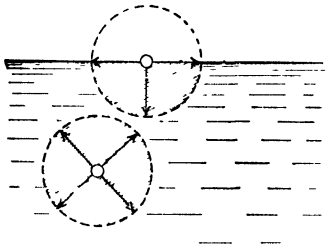


FIG 123.—Diagram indicating the range of molecular forces in a liquid

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 the attractive forces is small; van der Waals calculated it to be of the order of 10^{-6} cm 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. 123). This resultant force gives rise to **surface tension.**

The attractive forces between molecules are not always exerted uniformly in all directions, but may proceed 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 Investigations of Rayleigh (1899) indicated that the thinnest oil films on water were unimolecular in thickness, and the formation of unimolecular films has been proved in many cases, notably by Langmuir (1917) and Harkins (from 1917). A drop of a solution of fatty acid or other insoluble substance in benzene is brought on a perfectly clean surface of water. The solvent evaporates, leaving an isolated patch of the film By bringing a strip of paraffined paper across the surface of the water so as to enclose the film between it and the sides of the trough, no resistance is encountered until the edges of the film touch the sides of the trough and the strip of paper. A

resistance is now observed The area of the film is then equal to the area, A, between the paper strip and the sides of the trough, and since the weight, w, of the film is known, the area, a, occupied by a single molecule in the unimolecular film is given by

$$a = AM/w\mathbf{N}_0,$$

where M is the molecular weight of the substance in the film and $\mathbf{N}_0$, Avogadro's constant The thickness t of the film can be calculated on the assumption that the density is the same as that of the substance in bulk, δ

$$\delta \,.\, At = w$$

It is found that for fatty acids a is practically the same with varying lengths of chains of carbon atoms, so that it is assumed that the molecule is orientated vertically on the water surface with the carboxyl group, COOH, of the acid immersed in the water and the carbon chain outside

Some molecules in a liquid possess more kinetic energy than the average Such molecules, approaching the surface, will have sufficient energy to break away from the attractive forces, and will proceed outwards into the space above the liquid. This is the phenomenon of **evaporation.**

Escape of molecules of higher kinetic energy than the average will 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, will 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, as many molecules leave the liquid as pass back again per second ; this is a condition corresponding with the saturation vapour pressure , it is a *kinetic equilibrium*, due to two opposite processes going on simultaneously at equal rates.

If the forces acting on liquid molecules are as shown in Fig. 123, the work done in bringing a molecule from the interior of the liquid to the surface will be half that required to remove it altogether from the liquid to the vapour space, the latter being measured by the latent heat of evaporation (Stefan, 1886). The translational kinetic energy of the molecule is the same in the liquid and vapour, since it depends only on the temperature.

Molecular weights of liquids.—Since the particles in a liquid move about as individuals, they possess definite molecular weights. Molecules of more than one kind may, of course, be present: those formed by the combination of simple molecules are called **associated molecules** *e.g.*, $(H_2O)_x$.

Attempts have been made to determine the **molecular weights of liquids** by measurements of surface tension The product $\sigma[V]^{\frac{2}{3}}$ where σ = surface tension, V = molecular volume = M/D (D = density), is proportional to the surface energy of 1 mol of liquid in the form of a sphere, and was called by Eotvos and by Ramsay and Shields the **molecular surface energy.** This decreases with temperature, $t°$ C , according to the equation.

$$\sigma\,[V]^{\frac{2}{3}} = k(t_c - t - 6),$$

where k is a constant and t_c is the critical temperature For most liquids k is approximately 2·12, but in some cases, as with water, alcohol, and acetic acid, it is smaller

For bromine, $\sigma = 44$ at 13° C , $t_c = 302\ 2$, $M = 160(Br_2)$, $D = 3\ 12$;

$$\therefore k = 44 \times \left(\frac{160}{3\ 12}\right)^{\frac{2}{3}} - (302{\cdot}2 - 13 - 6) = 2\ 145$$

Since this is very nearly 2 12, bromine can be assumed to be normal

For water, $\sigma = 73$ at 15° C , $t_c = 370$, $M = 18$, $D = 1$, hence

$$k = 73 \times (18)^{\frac{2}{3}} \div (370 - 15 - 6) = 1{\cdot}497.$$

This is smaller than the normal value, 2·12 If we assume the molecular weight of water to be $x \times 18$, where x = **degree of association,** we may expect to get the normal value of k (since $18x$ is the true molecular weight), hence by division

$$x^{\frac{2}{3}} = 2\ 12/1{\cdot}497\ ; \quad \therefore\ x = 1{\cdot}69.$$

This result indicates that liquid water is associated

In some cases (*e g* , fused metals) the method leads to values of x smaller than 1, which are difficult to interpret

Another method which indicates association is the value of the **Trouton coefficient,** ML_e/T_o, where L_e is the latent heat of evaporation, and T_o the boiling point in degrees Abs For normal liquids this is about 21, for associated liquids it is larger, *e g* , 26·9 for alcohol and 25 9 for water

Solids.—In the solid state it is assumed that each molecule is performing oscillations of small amplitude about its fixed position of equilibrium. When heat is imparted to the solid, the amplitudes of these oscillations increase, and at a certain temperature the oscillations are so large that the molecules collide with each other, and break loose. This is the point of fusion 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. Since the solid is very little compressible, there must also be repulsive forces between the molecules, which increase more rapidly than the attractive forces when the distances between the

molecules are reduced. In its ordinary state, these two sets of forces are in equilibrium in a solid.

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 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 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

The question as to the **molecular weight** of a solid has little or no significance, since the particles composing the solid crystal may not correspond with the molecular formula of the substance. In sodium chloride crystals, for example, the individual particles are charged sodium and chlorine atoms (**ions**), Na^+ and Cl^-, not molecules, NaCl, and a diamond crystal consists of single atoms of carbon linked together by strong forces to which the hardness and low volatility of the substance are due The old idea that the solid state indicated a high molecular weight, and polymerisation, so that the molecules in diamond were C_n, for example, is definitely incorrect. The solid state will be considered in detail later

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 fixed ratio to that in the gas-space, as required by Henry's law. A state of kinetic equilibrium is set up: Gas $\rightleftharpoons$ Gas (dissd.), with 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 220) $=\frac{1}{2}D\times\frac{1}{2}\Omega=DG/\sqrt{6\pi}=0\cdot230DG$ In the case of oxygen at S T P, $D=0\cdot001429$ gm per c c, $G=4\cdot61\times10^4$ cm. per sec, .. the mass of oxygen striking 1 sq cm of the liquid surface per second is $0\cdot230\times0\cdot001429\times4\cdot61\times10^4$ gm $=15\cdot1$ gm This contains

$$\frac{15\cdot1}{32\times1\cdot66\times10^{-24}}=2\cdot85\times10^{23}\text{ molecules,}$$

or the number in about 10 litres

A proportion at least of the impinging gas molecules passes through the surface into the liquid, owing to molecular attraction between them and molecules of the liquid. Some of the gas molecules moving in the liquid will be approaching the surface, and if the kinetic energy of one

of these is sufficiently above the average value, it will leave again into the gas-space. This occurs the oftener the more gas molecules are dissolved. A state of kinetic equilibrium is reached when equal numbers of molecules leave and enter the liquid per second.

When the pressure of the gas is raised, the number of molecules per c c. is increased, and the number striking the surface becomes larger in the same ratio. The number of molecules per c.c. in the liquid is also increased. Hence more molecules leave the liquid than previously. When equilibrium is established, the same number leave as enter per second, but if the number entering is increased n times the number per c c of liquid also increases 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 in a saturated solution molecules are caught into positions of oscillation. In this case the kinetic nature of the equilibrium 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. Ultramicroscopic investigations (Traube and v. Behren, 1928) show that, in dissolving, a crystal is often resolved into small aggregates of molecules, **submicrons**, which then disperse as molecules or ions after a very short interval. In the formation of crystals the reverse process occurs, strings of submicrons building up small " blocks," of which the crystal aggregate consists.

Attempts have been made to find the radii of particles in solutions by assuming them to be spheres and applying Stokes's law

$$v = \frac{1}{6\pi\eta r},$$

where v is the mobility (=speed under unit force on the particle) and η the viscosity of the liquid. The force acting on the particle may be osmotic pressure as in the case of diffusion, or an electric potential gradient as in the case of a migrating ion, or both combined, as in the diffusion of ions This method gives certain results only for large (colloidal) particles.

The Parachor.—For a non-associating liquid the influence of temperature on the surface tension σ is given by the relation $M\sigma^{\frac{1}{4}}/(D-d) = \text{const} = P$, where D and d are the densities of liquid and vapour and M = mol wt In many cases d can be neglected P is called by Sugden the **parachor,** and is interpreted as the molecular volume measured at a standard internal pressure The parachor is very approximately additively composed of a sum of terms for the separate atoms together with constants for the particular forms of linkages Double bonds, rings, etc , have characteristic values, so that the parachor enables conclusions to be drawn as to the constitution of molecules The values of the parachor constants are H = 17 1 , C = 4 8, N = 12·5 , O = 20 0 , F = 25 7 , Cl = 54 3 , Br = 68 0 , I = 91 0 , S = 48 2 , P = 37 7 , Si = 28 , single bond arbitrarily taken as zero , double bond = 23 2 , triple bond = 46 6 In the case of compounds containing double bonds it is found that these fall into two classes, one giving normal results with the value 23 2, and the other showing a small *decrease* in parachor of about 1 6 units The second class contains semipolar double bonds (p 352), *i e* , coordinate links which give rise to a small decrease in parachor volume owing to the electrostatic attraction between the two charges The singlet linkage, formed by a single electron, has a parachor of −11 6, and a semipolar single bond, in which an atom is held by a singlet link but is at the same time in a state of incipient dissociation, has a value of −12·4.

SUMMARY OF CHAPTER XV

The molecules of gases, at temperatures above the absolute zero, are in motion They 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 is given by: $p = \frac{1}{3}DG^2$ The **mean speed,** Ω, is $0\cdot921\sqrt{G^2}$ At 0° C. 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 speed is proportional to the square root of the absolute temperature.

The **kinetic energy of translation** of the molecules in 1 mol of gas is $\frac{1}{2}MG^2$, where M = mol wt , this depends only on the temperature and is the same for all gases At 0° C. it is $3\cdot41 \times 10^{10}$ 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, $\mathbf{N_0}$, is the number of molecules in a mol ; with a probable accuracy of 1 per cent it is $\mathbf{6\,06 \times 10^{23}}$

The molecules of liquids and solids are much closer together than those of gases, and exert forces on one another.

CHAPTER XVI

ELECTROLYSIS

The dualistic theory of Berzelius.—Lavoisier showed that non-metals (except hydrogen), when burnt in oxygen, yield acidic oxides which produce 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, a basic oxide, is mixed with the acidic sulphur trioxide, both 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 the **dualistic system.**

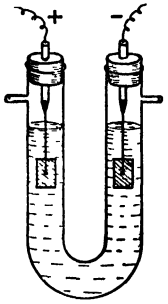


FIG 124.—U-tube with electrodes

Berzelius found that solutions of the salts of the alkalies, when decomposed by an electric current, liberate alkali at the negative pole and acid at the positive pole, and he considered that the alkali and acid possessed positive and negative charges, respectively, and were drawn to the poles by the attraction of unlike charges.

EXPT. 1.—Pour a solution of sodium sulphate, coloured purple with neutral litmus, into a U-tube with electrodes (Fig 124), and connect with a battery. The liquid around the positive pole becomes red, showing that an acid (sulphuric acid) is set free, whilst that surrounding the negative pole becomes blue, from liberation of alkali (caustic soda). Oxygen and hydrogen are liberated at these poles, respectively.

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:

$$\text{Sulphate of soda } \overset{+}{Na_2}O,\overset{-}{SO_3}.$$

$$\text{Soda } \overset{+}{Na_2} + \overset{-}{O}. \qquad \text{Sulphuric acid } \overset{+}{S} + \overset{-}{O_3}.$$

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. 111.

This dualistic system in its original form was soon shown to be untenable 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:

$$\underset{\text{Acetic acid}}{C_2H_4O_2} + Cl_2 = \underset{\text{Chloroacetic acid}}{C_2H_3ClO_2} + HCl.$$

Many complicated equations involving oxidation and reduction are, however, most simply written down by making use of the obsolete dualistic notation, and the latter is still of service in this way.

For example, the oxidation of ferrous salts by acidified permanganate or dichromate solutions may be represented as an oxidation of $2FeO$ to Fe_2O_3, and a reduction of MnO_4 to MnO or of $2CrO_3$ to Cr_2O_3 (see pp 216, 937, 952) The dualistic notation is also frequently used in representing the composition of minerals, *e g*, felspar, $K_2O,Al_2O_3,6SiO_2$

The electrolysis of sodium chloride solution.—Although the liberation of chlorine at the anode in the electrolysis of common salt could be explained by Berzelius's dualistic theory, since the oxygen usually liberated with salt solutions (Expt. 1) could be assumed to form oxymuriatic acid (chlorine) with the muriatic acid set free, the facts are better explained by assuming that sodium and chlorine are the actual products of electrolysis. $NaCl = Na + Cl$

EXPT 2.—Repeat Expt 1, 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 as if the salt is decomposed with liberation of chlorine, and the sodium 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 3.—Pour mercury into a glass tube having a platinum wire sealed through the bottom (Fig 125) 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.

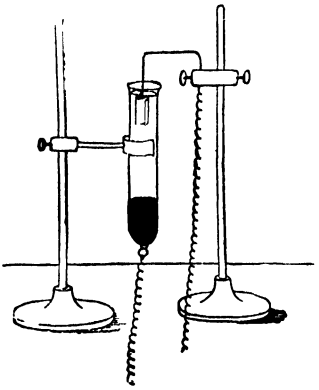


FIG 125 —Electrolysis with mercury cathode

It may be assumed that the current in Expt. 2 causes the deposition of sodium and chlorine 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 :

$$\text{Neg. pole } H_2 + 2NaOH \leftarrow 2H_2O + 2Na \quad \overset{2NaCl}{\downarrow \quad \searrow} \quad 2Cl \rightarrow Cl_2 \text{ gas Pos. pole.}$$

The **primary products** of the electrolysis are thus supposed to be 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 in this way, and that the acid and base, regarded as primary products by Berzelius, were really secondary products Sodium sulphate he regarded, following Davy, 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_2SO_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 :

$$\underset{\text{Neg pole}}{H_2 + 2NaOH \leftarrow 2H_2O + 2Na} \quad \overset{Na_2SO_4}{\downarrow \quad \searrow} \quad \underset{\text{Pos pole}}{SO_4 + H_2O \rightarrow H_2SO_4 + O}$$

All salts were, therefore, 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 salts of hydrogen. Daniell's theory was generally adopted, and the theory of Berzelius was given up. The theory of primary and

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secondary products of electrolysis just given has been modified as a result of experiments of Le Blanc. He considers that the liberation of hydrogen and oxygen from sodium sulphate solution occurs owing to a *primary* decomposition of water, the other constituent of which forms the alkali and acid, respectively, at the two electrodes. The hydrogen and oxygen (the latter really coming from a secondary reaction between discharged OH) are thus primary products. This theory will be explained in greater detail later.

Electrolysis.—The laws of electrolysis were discovered by Michael Faraday, in 1832–33. He introduced a number of new names, really due to Whewell, which are still used in describing the phenomena.

Conductors of electricity are of two kinds · (1) those which conduct the current without undergoing chemical change, and are simply heated by the current; metals and graphite belong to this class of **metallic conductors**: (2) those which are decomposed by the current, such as acidulated water, and solutions of salts, called **electrolytes** (Greek *lysis*, setting free). This name is now used to denote also the dissolved substances themselves; common salt and sulphuric acid are called electrolytes because when dissolved in water they form electrolytically conducting solutions In electrolysis one portion of the electrolyte 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) The parts of the electrolyte which move to the electrodes are called **ions** (*ἰών*, part of the verb *ἰέναι*, to go, used by Homer); the **anions** arrive at the anode and the **cations** at the cathode No chemical action is perceptible in the body of the electrolyte, but only at the electrodes, since only at these are the ions moving through the liquid liberated (Fig. 126)

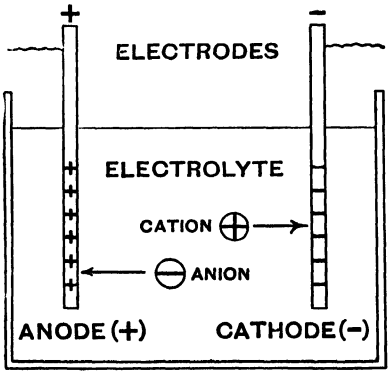


FIG 126 —Nomenclature of electrolysis

Faraday's laws of electrolysis.—The quantitative laws of electrolysis, relating the masses of the ions deposited to the charge transported through the electrolyte, were discovered by Faraday * In his first memoir (1832) he made out the relation between the mass of any particular ion deposited and the amount of electricity required for its deposition. The two were proportional, or in Faraday's words · "*the chemical action of a current of electricity is in direct proportion to the absolute quantity of electricity which passes.*" This is the **first law of electrolysis.**

In his second memoir (1833) he made out the relation between the masses of various ions deposited by the same quantity of electricity. These were in the ratios of the chemical equivalents

Since galvanometers and units of current were then not related, Faraday used the amount of gas produced by the electrolysis of

* *Experimental Researches in Electricity*; reprinted in *Everyman's Library*

acidulated water as a measure of the quantity of electricity which passes, and he determined the quantities of other elements liberated in electrolysis by the same current as liberates 1 gram of hydrogen

These quantities were the ordinary chemical equivalents, and hence he discovered the **second law of electrolysis** · *the weights of the ions deposited by the passage of the same quantity of electricity are in the proportion of their chemical equivalents*

To illustrate Faraday's laws we may connect in series a number of electrolytic cells, containing different electrolytes, with a battery as shown in Fig 127. Suppose 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.

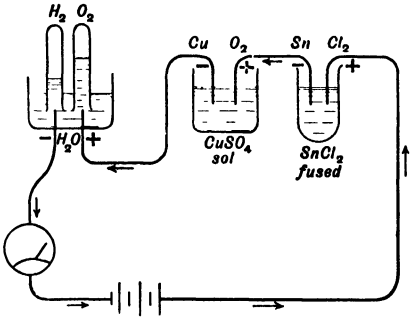


FIG 127.—Diagram of electrolytic circuit

After the current has passed for a certain time, 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, are ascertained. 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, they are found to be equivalent weights. 7·94 gm. of oxygen, 35·2 gm of chlorine, 31·5 gm of copper and 59 gm. of tin

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. 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.

The **international ampere** is defined as that current which, flowing uniformly for 1 second, deposits under specified conditions 0·001118 grams of silver from a solution of silver nitrate. This is called the **electrochemical equivalent** of silver; the weight z gm of any ion deposited by 1 coulomb is its electrochemical equivalent; hence the weight deposited by a uniform current of C amperes flowing for t seconds is:

$$W = Czt.$$

Since the chemical equivalent of silver (O = 16·000) is 107·880, the quantity of electricity required to deposit this amount will be (by Faraday's first law) 107·880/0·001118 = 96,500 coulombs per gm. equiv very nearly. This fundamental charge is called a **faraday**, denoted by *F*.* Faraday's second law shows that 1*F* will deposit 1 chemical equivalent of *any* ion Since Faraday's law will enable us to find the equivalent of an element (*e.g.*, oxygen, copper, silver), it will enable us to determine the valency of the element in the state of the ion investigated valency = at wt / equivalent (p 215)

The laws of electrolysis are conveniently summarised in the statement that *96,500 coulombs liberate one gram-equivalent of any ion in electrolysis*

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 25 × 60 × 60 = 900 cmb

Copper is bivalent, hence equivalent weight = at wt −2 = 63·5/2 = 31 75

96,500 cmb liberate 31 7 gm of Cu, hence wt of copper liberated by 900 cmb = 31·75 × 900/96,500 = 2 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 move to the electrodes, it is simplest to assume that they are attracted by the electrodes and are themselves charged, the sign of the charge on an ion being opposite to that of the electrode towards which it moves. Anions are negatively charged atoms or radicals: cations are positively charged atoms or radicals In the electrolyte two streams of charged ions move in opposite directions to the two electrodes (Fig. 128). These streams of charged ions constitute the current; 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 When a negative anion touches the anode, its charge passes into the latter, which is able to conduct the electricity without simultaneous movement of ions. The positive cation touching the cathode neutralises its charge, and the two

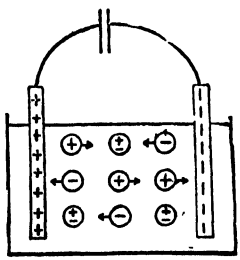


FIG 128 —Migration of ions in electrolytic cell

* Not to be confused with the farad, the unit of electric capacity

uncharged atoms or molecules are liberated at the electrodes They may then react with the water to form secondary products. The strength of the current is uniform throughout the whole circuit, whether the latter is all metallic or composed of metal 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

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 A univalent cation such as sodium carries one unit positive charge, a bivalent cation such as copper carries two unit positive charges A univalent anion, such as chlorine, carries one unit negative charge, equal in magnitude but opposite in sign to the charge on a univalent cation, whilst a bivalent anion such as the sulphuric acid radical, SO_4, carries two unit negative charges, and so on

The ionic charges carry 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.

Faraday (1833) had remarked that the second law would be explained on the assumption that "the atoms of bodies which are equivalents to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them," but he hastens to state that he does not believe in the existence of atoms

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^{14} tons weight. As Faraday remarks, the electric charges concerned in the most violent flash of lighting 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 Faraday, as we have seen, and was revived by Maxwell in 1874 Both expressed scepticism as to the atomic nature of electricity. In 1874, in a paper read to the British Association (not published until 1881) G. Johnstone Stoney calculated the charge associated with the hydrogen atom Since the charge on 1·008 gm. of hydrogen is 96,500 coulombs, and since this amount of hydrogen contains $6{\cdot}06 \times 10^{23}$ atoms, the unit charge is

$$96{,}500/6{\cdot}06 \times 10^{23} = 1{\cdot}592 \times 10^{-19} \text{ coulomb},$$

or (since 1 coulomb $= 3 \times 10^9$ electrostatic units), it is $4{\cdot}776 \times 10^{-10}$ E S.U Stoney called this atomic charge the **electron**

J J Thomson, in 1895, showed that the *negative* electron exists in the free state in Crookes's cathode rays (p. 416), and it moves free by conduction in metals. The positive electron (**positron**), with the same mass but opposite charge to the negative electron (**negatron** ; usually simply " electron "), has only a very transient existence, and the positive charge of smallest mass capable of prolonged independent existence is the **proton**, which is the nucleus of the hydrogen atom It is possible that the proton is not a primary particle, but is an association of a positron with a neutral particle, called a **neutron**, of mass almost equal to that of the hydrogen nucleus

One proton and one electron at some distance from it constitute the neutral hydrogen atom The positive **hydrogen ion** (or **hydrion**) existing in solution is not the proton, but is a solvated proton, *i. e.* one associated with one or more molecules of solvent The positive nuclei of other atoms contain both protons and electrons, with external electrons to produce neutrality of charge, and according as the number of external electrons is less than or greater than in the neutral atom, a positive ion (cation) or negative ion (anion) is produced. A negative ion is an atom or radical plus one or more electrons , a positive ion an atom or radical minus one or more electrons The charge of an ion may be represented by dots or dashes placed over the symbol ; one dot denotes unit positive charge, one dash unit negative charge $\dot{Cl}^-$, $\dot{H}^+$, Cu^{++}, SO_4^{--} may, therefore, be written as $\dot{Cl}'$, $\dot{H}$, $\dot{Cu}$, SO_4''. Another system of representing ions is Sn^{4+}, $FeC_6N_6^{4-}$, etc. All these methods will be used in what follows

The electron at rest has a mass of 1/1845 that of a hydrogen atom, *i.e.*,

$$1{\cdot}66 \times 10^{-24}/1845 = 8{\cdot}9 \times 10^{-28} \text{ gm.},$$

and its radius, assuming it to be a sphere, is $1{\cdot}9 \times 10^{-13}$ cm ; the hydrogen atom is $1{\cdot}2 \times 10^{-8}/1{\cdot}9 \times 10^{-13} = 6{\cdot}32 \times 10^4$ times the diameter of the electron.

The electronic charge.—The value of the charge on the electron has been determined in different ways, notably by the American physicist, R. A. Millikan (1912), who used the following very direct method.

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 above 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 electrically charged A particular drop was focussed in the field of a microscope with a scale in the eyepiece, as shown diagrammatically in Fig 129 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 ratio of the velocities with and without the potential difference, the charge on the drop could be calculated

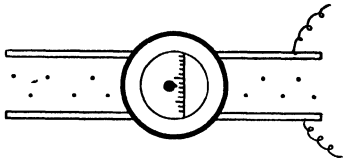


FIG 129.—Millikan's determination of the electronic charge

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 $1\cdot59\times10^{-19}$ coulombs Thus, *the charge on the electron is* $1\cdot59\times10^{-19}$ *coulombs.*

The value of the charge can be determined in other ways The value determined by Rutherford and Geiger by counting the α-particles emitted from radium (p 225), was $1\cdot55\times10^{-19}$ cmb, but Millikan's value is probably more accurate

Electrolytic dissociation.—The picture of the mechanism of electrolytic conduction employed above suggests that ions move independently through an 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.

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 his **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

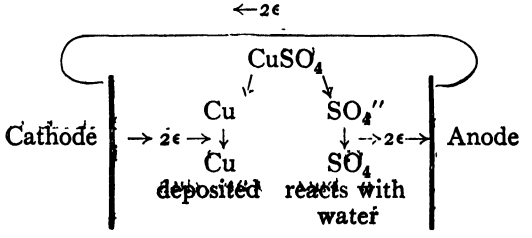
methyl alcohols, pyridine, anhydrous hydrocyanic acid, or formamide), undergoes change in such a way that from the electrically neutral molecule two or more charged ions are produced. The sum of the positive and negative charges on the ions must always be zero, since the solution as a whole is uncharged.

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 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 electronic 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 electrons which have passed round the metallic wire circuit from the chloride ions discharged at the anode, 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 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

The electrolytic dissociation, or ionisation, of a dissolved electrolyte is different from the thermal dissociation of a gas. 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: $NH_4Cl = NH_4^{\cdot} + Cl'$.

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 was asked Arrhenius 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 is 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^{2+}. and the ferric ion, Fe^{3+} The addition of unit positive charge alters the properties of the ferrous ion, and it is reasonable to suppose that the properties of sodium and chlorine atoms are also 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^{2+}. When this is converted into the ferric ion another electron is removed, producing Fe^{3+}. This corresponds with **oxidation**, since increase of positive valency occurs Increasing the valency of a cation, or its oxidation, therefore corresponds with increasing its positive charge. **Reduction** is equivalent to diminution of positive charge on an ion, or increase of negative charge. Ferricyanides are reduced to ferrocyanides by increasing the negative charge on the ion by one unit: $Fe(CN)_6^{3-} + \epsilon = Fe(CN)_6^{4-}$. Iron treated with chlorine water 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: $3Cl + 3\epsilon = 3Cl'$.

The **electrovalency** of an ion is equal to its charge; $+3$ for the ferric ion or -4 for the ferrocyanide ion. It represents the number of electrons lost or gained by the neutral atom in forming the ion. This is an extension of the elementary idea of valency, since sodium chloride in solution is not Na – Cl, but Na^+ and Cl^-, two separate ions.

Diffusion potential.—Another criticism advanced against the theory of electrolytic dissociation was that, if the ions are free in the solution, it should be possible to separate them. The answer is that such a separation can, in fact, occur. 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 direct measurements of the speeds of ions in a potential gradient, 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 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 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.

Reactions between ions.—Since most salts are extensively ionised in solution, the reactions between them usually occur between ions On adding a solution of sodium chloride to one of silver nitrate, the silver ion and chloride ion form insoluble silver chloride, which is precipitated, whilst the sodium and nitrate ions take no part in the reaction Instead of the equation $AgNO_3 + NaCl = AgCl + NaNO_3$, therefore, a more correct representation is $Ag^{\cdot} + NO_3' + Na^{\cdot} + Cl' = AgCl + Na^{\cdot} + NO_3'$, or, since the sodium and nitrate ions are not concerned, the **ionic equation** $Ag^{\cdot} + Cl' = AgCl$. A necessary condition for the correctness of an ionic equation is that the sum of the positive and negative ionic charges shall be the same on both sides

$$Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu \text{ (p 864)},$$
$$2Fe(CN)_6'''' + Cl_2 = 2Fe(CN)_6''' + 2Cl' \text{ (p 977)},$$
$$Fe(CN)_6'''' + 12H^{\cdot} + 6H_2O = Fe^{\cdot\cdot} + 6NH_4 + 6CO \text{ (p 689)}$$

The ionisation of electrolytes.—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 mol of water ionised in ten million litres (10^{10} c c)

If 1 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 ten millionfold. This great increase in conductivity is due to the ionisation of the hydrochloric acid: $HCl \rightleftharpoons H^{\cdot} + Cl'$, the ions of which are present in very great numbers as compared with the ions of water. The acid, in fact, exists in the solution almost completely in the form of ions. Hydrochloric acid is a **strong electrolyte**, water is a very **weak electrolyte.**

Most acids, bases, and salts, such as hydrochloric acid, sulphuric

acid, caustic potash, lime, common salt, copper sulphate, and alum, give conducting solutions with water, and are electrolytes Pure sugar, urea, alcohol, and most organic compounds, 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 *most salts are electrolytes*, whilst substances which are not salts are non-electrolytes

All acids give the hydrogen ion in aqueous solution 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.

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 130 (Nernst)

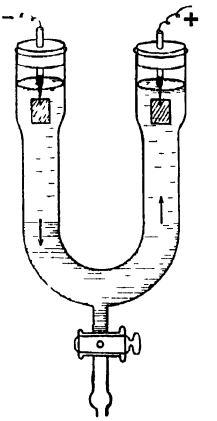


FIG 130 —Demonstration of ionic migration

EXPT 4 —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 D C mains The purple MnO_4'-ions at once begin to move towards the anode, and the levels alter in the directions shown If the former levels are marked by thin strips of gummed label, the change is quite apparent after 10–15 minutes

This experiment shows that the speed of the ions in bulk through the solution is very slow It thus resembles the diffusion of dissolved substances. In both cases the moving particles enter repeatedly into collision with the molecules of the solvent The actual **ionic mobilities**, under a potential gradient of 1 volt per cm., 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) are given below ·

$K^{\cdot}$	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'	0·00069
		$NH_4^{\cdot}$	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).

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 (as is seen from the table above), it carries most of the current, and the relative conductivities of different acids are therefore approximately proportional to the ionisations.

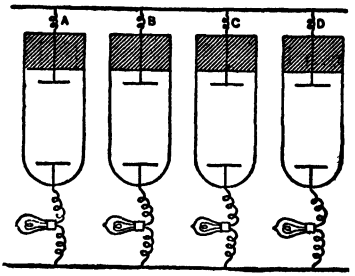


FIG 131.—Comparison of conductivities of acids

EXPT 5.—Distilled water and $N/50$ solutions of acetic, sulphuric, and hydrochloric acids are poured into four glass tubes, fitted with electrodes (Fig 131). The electrodes are the same distance apart in the three tubes, and in series with each tube is a carbon-filament lamp. The tubes are connected in parallel with the mains. The lamps in circuit with the water and acetic acid remain dark, because the conductivities are 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 149).

Equivalent conductivity.—If a cell is formed containing two platinum electrodes 1 cm^2 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.

The conductivity of a solution depends 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 $\frac{1}{2}CuSO_4$), 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 be ionised To make a fair comparison between the ionisations of these various solutions we must divide the conductivity k by the number of gm equiv of salt *per c c.* in the solution, c, and the quotient k/c is called the **equivalent conductivity,** denoted by Λ Thus $\Lambda = k/c$

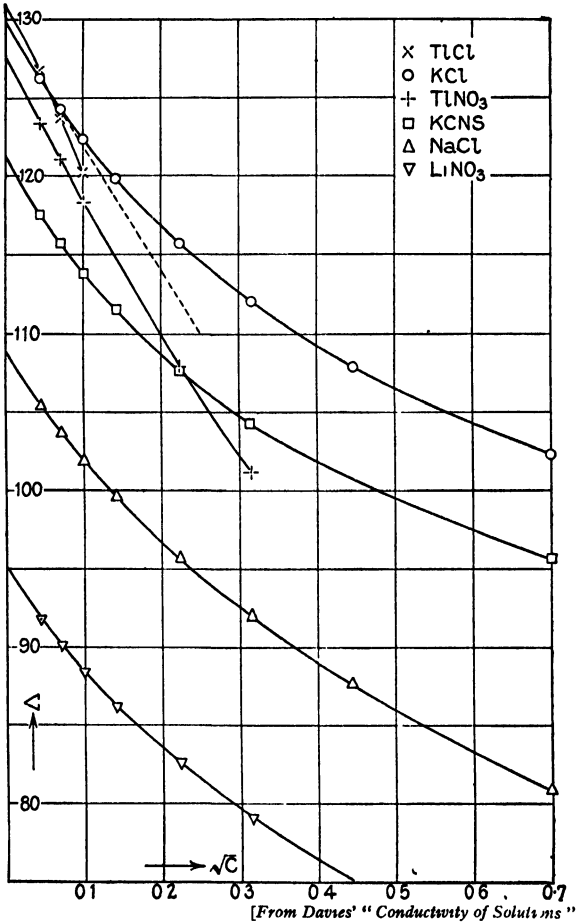
Thus, if we have 1 gm equiv in 10^6 litres practically completely ionised, giving a certain conductivity k_1, and we then dilute the solution to 10^{10} litres, we obtain a smaller conductivity, k_2 But if we imagine all the ions present to be collected into 1 c c in each case, we should have two identical solutions, since the numbers of ions are equal, and thus Λ is the same for both

It is found by experiment that the equivalent conductivity of an electrolyte increases gradually with the dilution The curves in Fig 132 show the equivalent conductivities of a few electrolytes plotted against the square root of the concentrations in gm equiv per *litre*

This result can be explained in two ways. It may be assumed that the electrolyte is completely dissociated into ions at all concentrations, but that the speeds of the ions carrying the current increase as the solution becomes more dilute, until in very dilute solution the ionic speeds (for a given potential gradient between the electrodes) become constant. Or it may be assumed that the speeds of the ions are practically constant at the various concentrations but the dissolved electrolyte is incompletely ionised, the ionisation increasing 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, corresponding with complete ionisation, is called the **equivalent conductivity at infinite dilution,** denoted by Λ_∞. Since there are now only ions in the solution, the ratio k/c, or Λ, has become constant.

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, gives, on the theory of incomplete ionisation, the **degree of ionisation,** α, corresponding with the given dilution : $\Lambda_v/\Lambda_\infty = \alpha$. The dilution is the reciprocal of concentration,

i e., v is the number of cm.^{3} 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.



[*From Davies' "Conductivity of Solutions"*

FIG 132.—Equivalent conductivities of uni-univalent salts (M'X') in water at 18°c

The change of Λ with dilution in the case of weak electrolytes (p. 248) is too large to be accounted for by varying mobility, and an increase of ionisation must be assumed.

The progressive ionisation of a typical weak electrolyte is seen from the table below.

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 $K = \alpha^2/(1-\alpha)v$
0 334	0 6186	0 0016	$7\,7 \times 10^{-6}$
1 977	2·211	0 0057	$16{\cdot}5 \times 10^{-6}$
10 753	5 361	0 0138	$18\,0 \times 10^{-6}$
63 26	13 03	0 0336	$18\,5 \times 10^{-6}$
∞	387 9	1 0000	—

Acetic acid is only slightly ionised, even in dilute solutions, and the increase in Λ with dilution is very largely due to the increasing ionisation of the acid.

Determination of conductivity.—If an ordinary current from a battery is passed between platinum electrodes in a solution of an electrolyte, and a galvanometer included in the circuit, the current strength diminishes as electrolysis proceeds. This 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 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 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.

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 The platinum black exposes a large surface

EXPT. 6.—A convenient type of **electrolytic cell,** shown on the right in Fig 133, consists of a small bottle, with parallel platinised platinum electrodes The wires from the electrodes, which are covered with glass inside the cell, pass into glass tubes containing mercury, and wires dip into the mercury to make contact These wires pass through rubber tubes, so that the cell may be immersed in a tank of water kept at a constant temperature, say 18° or 25°.

Since a galvanometer cannot be used with an alternating current, a telephone is employed. A resistance-box is connected with the cell,

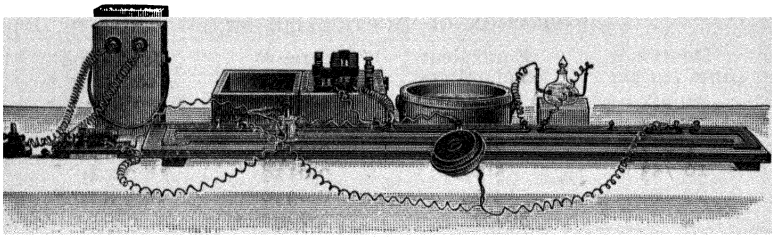


FIG. 133.—Apparatus for measurement of conductivity.

telephone, coil, and a metre wire-bridge with a scale and sliding contact. The connections are shown in Fig. 134.

The slider is placed near the middle of the bridge, plugs are taken out of the box until the sound in the telephone is appreciably reduced, and the slider is moved until the sound in the telephone is a minimum.

The resistance of the conductivity cell is given by the Wheatstone bridge formula $\frac{R}{r} = \frac{a}{100-a}$; $\therefore r = R \times \frac{100-a}{a}$ ohms. Ohm's law has been proved experimentally to apply to electrolytes. The **conductance** is $1/r$, *i.e.* the current passing in amperes for 1 volt potential difference between the electrodes.

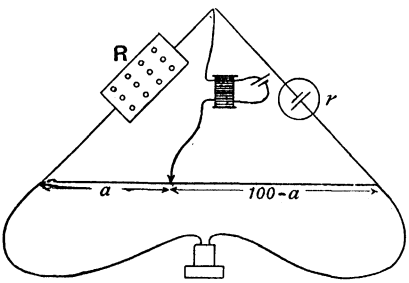


FIG. 134.—Diagram of conductivity apparatus.

The electrodes of the conductivity cell will not usually be exactly 1 cm.^{2} in area, parallel, and 1 cm. apart, so that the conductance, $1/r$, is not usually equal to the conductivity k. Since the relation between the two depends only on the construction of the cell, it is possible to determine this once for all by using as electrolyte a solution of known conductivity, viz., a normal solution of potassium chloride (74·555 gm. per litre, weighed in air), for which at 18° $k_{18°} = 0{\cdot}09822$. If the resistance of the cell containing this solution is r, $k_{18°} = C/r = 0{\cdot}09822$, where C is the **cell constant**. If any other solution is used, and if the resistance is r' ohms, the conductivity is $k'_{18°} = C/r'$.

Kohlrausch's law.—The independent movement of the ions of a salt assumed in the theory of electrolytic dissociation provides a simple

explanation of a result discovered experimentally by F. Kohlrausch in 1875, viz., that *the equivalent conductivity of a salt at infinite dilution is the sum of two parts, one depending only on the cation and the other only on the anion*:

$$\Lambda_\infty = l_c + l_a$$

This is known as **Kohlrausch's law.** For example:

	Λ_∞		Λ_∞
KCl	130·0	NaCl	108·9
KNO_3	126·3	$NaNO_3$	105·2
$\Lambda_\infty KCl - \Lambda_\infty KNO_3 = 3{\cdot}7$		$\Lambda_\infty NaCl - \Lambda_\infty NaNO_3 = 3{\cdot}7$	
$\Lambda_\infty KCl - \Lambda_\infty NaCl = 21{\cdot}1$		$\Lambda_\infty KNO_3 - \Lambda_\infty NaNO_3 = 21{\cdot}1$.	

The value 3·7 is the difference in l_a values for Cl and NO_3, and the value 21·1 is the difference in l_c values for K and Na. l_a and l_c are called the **mobilities** of the anion and cation, respectively, expressed in conductivity units.

The migration of ions.—The unequal speeds of different ions moving through an electrolyte in the same potential gradient causes changes of concentration of *salt* (not ions separately) around the electrodes. These changes, noticed by Gmelin in 1838 and by Daniell and Miller in 1844, were first fully investigated and related to the ionic speeds by Hittorf (1853).

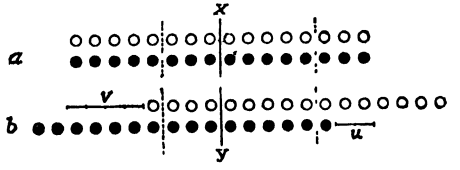


FIG. 135.—Migration of ions.

In Fig. 135 the black and white circles represent the cations and anions, in the upper row *a* before electrolysis and in the lower row *b* after. The black circles move to the left with a speed u and the white circles to the right with a speed v which is, in the case considered, twice as great as u. The vertical line XY divides the original arrangement into two equal parts.

Before electrolysis there are eight black and white ions on each side. After electrolysis, when six equivalents of salt have been decomposed and the unpaired ions deposited, there are four undecomposed equivalents of salt on the left and six on the right, so that four equivalents of salt have been lost on the left and two on the right. *The losses in neutral salt molecules around the electrodes are in the ratio of the speeds of the ions migrating away from the electrodes.*

The fractions of the total current carried by the cation and anion, respectively, are one third and two thirds, or, generally

$$u/(u+v) \quad \text{and} \quad v/(u+v)$$

or, since the total current Λ_∞ is the sum of l_c and l_a:

$$l_c/\Lambda_\infty = u/(u+v)\,; \quad l_a/\Lambda_\infty = v/(u+v)$$

The fraction of the total current carried by one ion is called the **transport number** of that ion, n. It is not a constant depending only on that ion, as the mobility is, but varies from salt to salt, according to the mobility of the other ion. If we refer n to the anion, then :

$$l_a/l_c = n/(1-n),$$

and from n and $\Lambda_\infty = l_c + l_a$, we can calculate l_c and l_a separately.

MOBILITIES IN AQUEOUS SOLUTION AT 18°.

Cations	l_c	Anions	l_a
Na	43·3	Cl′	65·3
K	64·5	Br′	67·3
$NH_4^{\cdot}$	64·5	I′	66·1
$H^{\cdot}$	315·6	NO_3'	61·6
Ag	54·0	OH′	174
$\frac{1}{2}Zn$	46·7	CH_3COO'	35
$\frac{1}{2}Cu^{\cdot\cdot}$	45·5	$\frac{1}{2}SO_4''$	67·9
$\frac{1}{2}Ba^{\cdot\cdot}$	55·0	$\frac{1}{2}CO_3''$	60

The large mobilities of the hydrogen and hydroxide ions should be noted

The value of Λ_∞ for a weak acid, such as acetic acid, is found by adding 315·6, the mobility of the hydrogen ion, to the mobility of the anion, *e.g.*, 35 for the acetate ion, CH_3COO',

$$\therefore \ \Lambda_\infty \text{ for acetic acid} = 315{\cdot}6 + 35 = 350{\cdot}6.$$

The specific conductivity, k, of saturated silver chloride solution at 18° is, after suitable correction by subtraction for the conductivity of the water used, $1{\cdot}24 \times 10^{-6}$ ohm^{-1} cm^{-1}, and since the solution is very dilute it may be considered completely ionised Now $\Lambda = k/c$, and in this case Λ may be taken as $\Lambda_\infty = 54{\cdot}0 + 65{\cdot}3 = 119{\cdot}3$, $\therefore \ c = 1{\cdot}24 \times 10^{-6}/1{\cdot}193 \times 10^{2} = 1{\cdot}04 \times 10^{-8}$ equiv per cm^3

Absolute speeds of ions.—Let a completely ionised solution of 1 equiv of salt be electrolysed with a potential gradient of 1 volt per cm. The ions move with speeds of u and v cm. per sec, and since the total charges on each kind of ion are $+F$ and $-F$, respectively, the charges transported per sec. are $+uF$ and $-vF$. Negative charge moving in one direction is equivalent to positive charge moving in the opposite direction, hence the total charge transported per sec. is $uF + vF$, which is the same as the current, viz, Λ_∞ or $l_c + l_a$. Hence :

$$l_c + l_a = F(u+v) \quad \text{or} \quad l_c = Fu \quad \text{and} \quad l_a = Fv.$$

Hence, since $F = 96{,}500$, the mobilities u and v in cm. per sec. for a potential gradient of 1 volt per cm. can be calculated from the values of l_c and l_a in the above table. In this way the values in the table on p. 249 were found : they are confirmed by direct measurements, as there described

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 ionised in solution, the reaction really occurs between the ions:

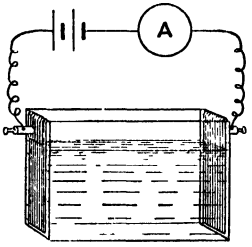


FIG 136.—Apparatus to demonstrate diminution in conductivity on neutralisation

$(H^{\cdot} + Cl') + (Na^{\cdot} + OH') = (Na^{\cdot} + Cl') + H_2O$ 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*: $H^{\cdot} + OH' = H_2O$ 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 ions and hydroxide ions are those which possess the greatest mobility. After neutralisation, therefore, when these ions have been withdrawn, the conductivity will be appreciably diminished.

EXPT 7.—Fit a rectangular glass trough with two electrodes of sheet copper (Fig 136) Connect these through an ammeter with two accumulators in series Pour into the cell *N*-caustic soda solution, containing urea to increase its density, and coloured with phenolphthalein Float a slice of cork on this solution, and by means of a burette 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.—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 union of hydrogen ions from the acid with hydroxide ions from the base to form practically undissociated water

This unexpected result is verified by experiment; the heat of neutralisation is, per equivalent of strong acid and base, equal to about 13·7 k. 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 85

If the acid or the base is weak the un-ionised acid or base will dissociate as neutralisation proceeds, and this dissociation will in general be attended by absorption or evolution of heat An example of this behaviour is the neutralisation of hydrofluoric acid If the salt formed is only slightly ionised (a very rare case), or is insoluble, the heat of neutralisation will also be abnormal, since association of the ions of the salt to form molecules, or precipitation of the salt, is attended by heat changes.

Theory of acids and bases.—In aqueous solutions of acids, the hydrogen ion is probably attached to a molecule of water, forming the hydroxonium ion, H_3O ; $H + H_2O = H_3O^{\cdot}$ Regarded as the result of the removal of an electron from a hydrogen atom, the ion H is the free proton, and this could scarcely be expected to exist in the free state in solution to any appreciable extent The hydrogen ion is probably also solvated in other media besides water

In the theory of acids and bases developed by Arrhenius, the hydroxide ion of bases occupies as unique a position as the hydrogen ion of acids Another theory, first developed by Lapworth (1908), defines a base as *a substance which unites with hydrogen ion*, or, in the more hypothetical terminology of modern theory, *a base is an acceptor of protons*, whilst *an acid is a donor of protons*. Whereas all acids must have a common property, this is not necessary in the case of bases. A neutral ammonia molecule may accept a proton to form the ammonium ion, and thus functions as a base :

$$NH_3 + H^{\cdot} = NH_4^{\cdot},$$

and this is just as much a neutralisation reaction as is the acceptance of a proton by the hydroxide ion :

$$OH' + H^{\cdot} = H_2O.$$

The NH_3 molecule may abstract protons from water :

$$NH_3 + H_2O \rightleftharpoons NH_4^{\cdot} + OH',$$

and in this case the greater strength of ammonia as compared with

water as a base is manifested by the appearance of OH' ions, *i e.*, by an alkaline reaction.

Lapworth's definition of bases shows that the acetate ion, CH_3COO^-, is a strong base, since when a strong acid such as hydrochloric, which is practically completely ionised, is added to solution of sodium acetate, largely ionised into Na^+ and CH_3COO^-, the acetate ions unite with practically all the hydrogen ions, forming the weakly ionised acetic acid molecules, CH_3COOH

The anion of any weak acid is, in fact, able to function as a strong base When a strong acid is neutralised with sodium carbonate the reaction is, *e g*,

$$\underbrace{2H^+ + SO_4^{--}} + \underbrace{2Na^+ + CO_3^{--}} = \underbrace{2Na^+ + SO_4^{--}} + H_2CO_3,$$

$$i\,e,\ 2H^+ + CO_3^{--} \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2 + H_2O$$

The weak carbonic acid is also unstable, and decomposes almost completely, carbon dioxide escaping with effervescence In aqueous solutions of sodium carbonate, the CO_3^{--} ions withdraw hydrogen ions from the water, forming the very weak carbonic acid and leaving hydroxide ions of the water, which make the solution alkaline and "basic"

$$CO_3^{--} + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^-$$

The real base is, however, not Na_2CO_3, but the carbonate ion, CO_3^{--}, a powerful hydrogen ion acceptor Reactions of this type are called **hydrolysis.**

Strong and weak electrolytes: Arrhenius's theory.—The current through a solution, or the charge transported per second, is proportional to the charges on the ions, the numbers of ions, and the speeds with which they move The charges on the ions remain constant, hence the increase in equivalent conductivity with dilution may be attributed to the increasing number of ions, *i e* increased dissociation, and the limiting value at infinite dilution to complete dissociation The **degree of ionisation** at any dilution will then be $\alpha = \Lambda/\Lambda_\infty$. This theory, due to Arrhenius, assumes that the speeds of the ions do not change on dilution

The tables below give the values of α for $0{\cdot}1N$ solutions at 18°, the ions produced being in brackets Electrolytes largely ionised at this dilution are called strong electrolytes (*e.g*, HCl), those slightly ionised are called weak electrolytes (*e.g.*, acetic acid).

Acids.		Bases	
Hydrochloric (H^+,Cl')	0 92	Sodium hydroxide (Na^+,OH')	0·91
Nitric (H^+,NO_3')	0 92	Potassium hydroxide (K^+,OH')	0 91
Sulphuric (H^+,HSO_4')	0·61	Barium hydroxide (Ba^{++},$2OH'$)	0·81
Phosphoric (H^+,H_2PO_4')	0 28	Ammonium hydroxide (NH_4^+,OH')	0·013
Hydrofluoric (H^+,F')	0 085		
Acetic (H^+,CH_3COO')	0·013		
Carbonic (H^+,HCO_3')	0·0017		
Hydrosulphuric (H^+,HS')	0·0007		
Boric (H^+,H_2BO_3')	0 0001		
Hydrocyanic (H^+,CN')	0·0001		

Whereas acids and bases differ considerably in strength, most salts are strong electrolytes, as the following table shows Sodium acetate is largely ionised, although acetic acid is weak ; ammonium chloride is a strong electrolyte, although ammonia is a weak base as measured by conductivity.

SALTS.

Potassium chloride ($K^{\cdot}$,Cl')	0 86	Sodium carbonate ($2Na^{\cdot}$,CO_3'')	0·70
Sodium chloride ($Na^{\cdot}$,Cl')	0 85	Zinc sulphate ($Zn^{\cdot\cdot}$,SO_4'')	0 40
Potassium nitrate ($K^{\cdot}$,NO_3')	0 83	Copper sulphate ($Cu^{\cdot\cdot}$,SO_4'')	0·39
Silver nitrate ($Ag^{\cdot}$,NO_3')	0 82	Mercuric chloride ($Hg^{\cdot\cdot}$,$2Cl'$)	< 0 01
Sodium acetate ($Na^{\cdot}$,CH_3COO')	0 80	Mercuric cyanide ($Hg^{\cdot\cdot}$,$2CN'$)	very small
Barium chloride ($Ba^{\cdot\cdot}$,$2Cl'$)	0 75		
Potassium sulphate ($2K^{\cdot}$,SO_4'')	0 73		

Modern theory of strong electrolytes.—The tendency of modern theory is to assume that strong electrolytes are practically completely ionised at dilutions greater than $0{\cdot}1N$ and that the change of conductivity with concentration is due, not to changes in the number of ions with constant speeds, as in Arrhenius's theory, but to changes of speed with constant number In the theory of Debye and Huckel (1923) the electrical forces between the charged ions are assumed to cause each ion to surround itself with an " atmosphere " of ions of opposite charge. When the ion moves it tends to leave this atmosphere behind, and to build up a new one, but owing to the slowness of motion (p 249) this takes time and there will be an excess of ions of opposite sign behind the moving ion, tending to drag it back This effect is greater the larger the concentration, hence the ions will move faster in more dilute solutions and the equivalent conductivity, Λ, will increase on dilution, until at infinite dilution, when the ionic forces are negligible, it reaches a constant value, Λ_∞. A second effect retarding the motion of the ions is due to the friction opposed by the solvent to the motion of the positive and negative ions composing the ion atmosphere about any central ion (see p. 250). This atmosphere must be dragged by the moving ion through the solvent, thus giving rise to retarding forces which also disappear, like the first effect, at infinite dilution when the frictional force on the central ion alone remains.

The theory shows that the equivalent conductivity Λ_∞, which would be shown if the ions exerted no action on one another, is reduced to the value $\Lambda = \Lambda_\infty - a\sqrt{c}$, where c = concentration and a is a constant, and Fig. 132 shows that Λ when plotted against the square-root of the concentration gives, at small concentrations, very nearly a straight line. This was discovered empirically by Kohlrausch many years ago. The theory shows that the slope of the Λ and $\sqrt{c}$ curves should be greater with ions of higher valency (*e.g.*, $Cu^{\cdot\cdot}$, SO_4'') and this also had been found by Kohlrausch.

Ionisation in stages.—Molecules capable of giving more than two ions often dissociate in stages, but this is not always the case. Potassium ferrocyanide, $K_4Fe(CN)_6$, ionises directly according to the equation: $K_4Fe(CN)_6 = 4K + Fe(CN)_6''''$, 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 a base, the hydrogen ion is completely eliminated, with the hydroxide ion of the base, in the form of water: $H_2SO_4 + 2OH' = SO_4'' + 2H_2O$. The reason for this 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 $H_2SO_4 = H + HSO_4'$, 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 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.

Water is principally ionised, to a slight extent only, into H and OH' (or perhaps into H_3O and OH') A further dissociation of OH' probably occurs to a very minute extent. $OH' \rightleftharpoons H + O''$.

It is almost always the case that the later stages of ionisation of polybasic acids are small; *e.g.*, with phosphoric acid

$$H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4' \rightleftharpoons 2H^{\cdot} + HPO_4'' \rightleftharpoons 3H + PO_4''',$$

the last stage is so slight that the PO_4''' ion in a phosphate such as Na_3PO_4 acts as a strong base

$$PO_4''' + H_2O \rightleftharpoons HPO_4'' + OH'.$$

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) 96,500 coulombs liberate 1 gm equiv. of any ion This quantity of electricity 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 $1{\cdot}59 \times 10^{-10}$ emb Free positive electrons are not known; a positive ion is an atom or radical which has lost one or more negative electrons and the smallest positive charge is the **proton,** or nucleus of the hydrogen atom.

The **conductivity**, k, 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 at a potential difference of 1 volt.

The **equivalent conductivity** of a solution is the conductivity divided by the concentration, c, in gm equiv per cm^3 $\Lambda = k/c$ It increases with dilution On the assumption that the ionic mobilities are independent of dilution, this result is explained as due to partial ionisation, on dilution the ionisation increases The **degree of ionisation** is measured by the ratio of the equiv conduct. at a given concentration to the equiv conduct at infinite dilution, corresponding with complete ionisation, $\alpha = \Lambda_v/\Lambda_\infty$ In the case of **strong electrolytes** (largely ionised) it is now assumed that ionisation is complete at all except fairly high concentrations, and the change of equivalent conductivity on dilution is explained as due to the retarding influence exerted by an atmosphere of ions around the central ion, containing an excess of ions of opposite charge, this influence on a moving ion increasing with the concentration c, according to the equation $\Lambda = \Lambda_\infty - a\sqrt{c}$ (Debye and Huckel).

Kohlrausch's law states that the value of Λ_∞ is additively composed of the **mobilities** of the cation and anion $\Lambda_\infty = l_c + l_a$ The ratio of the current carried by an ion to the total current is called the **transport number** *e g*, $n = l_a/(l_a + l_c)$ It may be measured by the changes of concentration of electrolyte occurring around an electrode, due to the unequal speeds of the two ions The **absolute speeds** of the ions, in cm. per sec. per volt per cm are given by $u = l_c F$, $v = l_a F$, they may be measured directly with coloured ions, and are small, of the order of 0 0005 cm./sec (except for the $H^\cdot$ ion, 0 00326, and OH' ion, 0 0018)

Neutralisation of a strong acid by a strong base in aqueous solution 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 In general, a **base** is a substance which unites with protons. *e g*, $NH_3 + H^\cdot = NH_4^\cdot$, $OH' + H^\cdot = H_2O$

CHAPTER XVII

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 *dilute* solution is proportional to the concentration (Watson, 1771; Blagden, 1788) With cane-sugar in water:

Gm mols of sugar in 1000 grams of water $=C$	Freezing point lowering $=D$	Ratio D/C
0 000344	0 000645	1·87
0 000995	0 001867	1 88
0 002303	0 004332	1 881
0 004278	0 007957	1·861
0 01026	0 01906	1 857
0 01841	0 03434	1 866
0 0365	0 06793	1 862

Raoult (1883) found experimentally that *if quantities proportional to the molecular weights of different substances are dissolved in identical weights of a solvent, the freezing points of the solutions are identical.* A molecular weight in grams of a substance dissolved in 1 kilogram of water depresses the freezing point of the latter by 1·858°. This is called the molecular depression of freezing point, Δ, for water.

The molecular depression varies with the solvent The values for some common solvents are as follows

	Δ	M. pt		Δ	M pt.
Water -	- 1 858°	0°	Formic acid	2 8°	8°
Acetic acid	- 3 9°	17°	Phenol	7·27°	40°
Benzene -	- 4 9°	5°	Camphor	40°	180°

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.

$$\Delta = \frac{RT_f^2}{1000L_f}.$$

For water: $L_f = 79{\cdot}74$, $T_f = 273$; also $R = 1{\cdot}988$ g. cal./1·°C.

$$\therefore\ \Delta = 1{\cdot}988 \times (273)^2/(79{\cdot}74 \times 1000) = 1{\cdot}858.$$

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 w 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 Watson's law that the two depressions are proportional to the two concentrations :

$$\therefore\ w : M = D : \Delta,$$

$$\text{hence } M = \frac{w\Delta}{D}.$$

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.

w = No. of gm of solute per 1000 gm of solvent = $1{\cdot}35 \times 1000/55$

D = observed depression = 16 750 − 16 132 = 0 618°

Δ = molecular depression for acetic acid = 3 9°

$$\text{Molecular weight of solute } M = \frac{w\Delta}{D} = \frac{1{\cdot}35 \times 1000 \times 3{\cdot}9}{55 \times 0\ 618} = 155$$

The molecular weight calculated from the vapour density is $CCl_4 = 153$, hence carbon tetrachloride has the same molecular weight in the state of vapour as in solution in acetic acid

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. 137. A very sensitive thermometer, called a **Beckmann thermometer**, D, is used, which has a large bulb and 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. The actual readings on the scale are of no consequence, only their *difference*, D, is required. About 20 gm of the solvent are weighed into the tube A, and a stirrer of bent wire introduced. The thermometer is fitted into the tube through a cork, so that the bulb is covered with the liquid.

The tube *A* is fitted through a cork into a large test-tube, *B*, which serves as an air-jacket, and prevents too rapid fall in temperature. The tube *B* is supported in 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 of the solution read off Suppose this to be 2·839°; then *D*, the depression of freezing point, is 3·216 − 2·839 = 0·377°.

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 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.

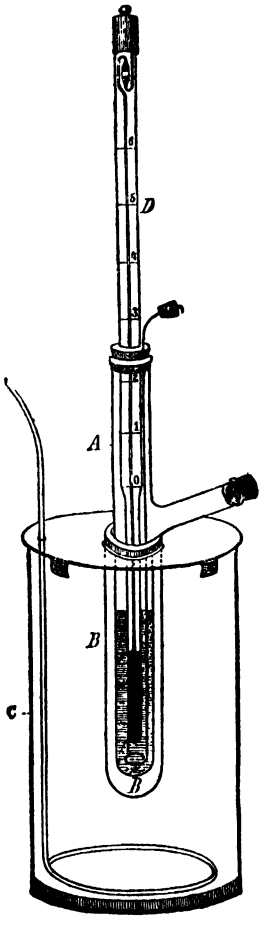


FIG 137 — Beckmann's freezing-point apparatus

Vapour pressures of solutions.—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; (4) the same for different solvents when the ratio of the number of mols of solute to the total number, solute plus solvent, is the same (Raoult, 1887).

The **molecular lowering of vapour pressure** is therefore a constant for a given solvent In a solution containing N 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 :

$$(f_0 - f)/f_0 = n/(N+n).$$

Thus, if 1 mol of solute is dissolved in 99 mols of solvent, there will be a lowering of vapour pressure of 1 per cent., since

$$n/(N+n) = 1/(99+1) = 0{\cdot}01.$$

The value of N is calculated from the weight of solvent taken divided by its molecular weight in the state of *vapour*, *i.e.*, N 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, $\therefore N = 100/78 = 1\ 282$ Also $(f_0 - f)/f_0 = (751{\cdot}86 - 742\ 6)/751\ 86 = 0\ 0123$, $\therefore$ $0\ 0123 = n/(1{\cdot}282 + n)$, $\therefore$ $n = 0\ 01598$ But $n = 2{\cdot}47/(\text{mol wt of ethyl benzoate})$, $\therefore$ mol wt. of dissolved ethyl benzoate $= 2{\cdot}47/0\ 01598 = 154{\cdot}5$. That calculated from the vapour density, or the formula $C_6H_5{\cdot}COO\,C_2H_5$, is 150.

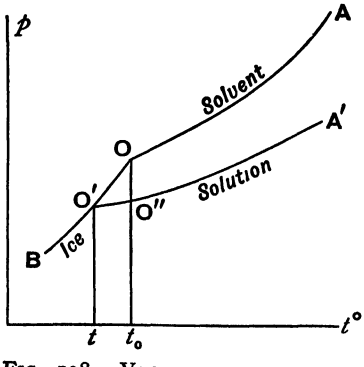


FIG. 138 —Vapour pressure curves of solvent, solution, and ice.

The connection between lowering of vapour pressure and depression of freezing point is shown in Fig 138. Let OA be the vapour pressure curve of the pure solvent At the temperature t_0 solvent freezes, and OB is the vapour pressure (sublimation) curve of ice. It has a different slope (much exaggerated in the figure) from OA The vapour pressure curve of the solution, O'A', lies below that of the solvent, and cuts the ice curve at O', corresponding with the freezing point of the solution, t, where solution and the separated pure ice are in equilibrium, each having the same vapour pressure If this were not the case distillation would occur between ice and solution and there could not be equilibrium.

Since O'A' lies below OA, O' will lie to the left of O, *i.e.*, $t < t_0$, or the freezing point is lowered as the vapour pressure is lowered For small depressions, OB and O'O'' may be regarded as straight lines and

OO'' is proportional to O'O'', *i e*, to $t_0 - t$ *The depression of freezing point is proportional to the lowering of vapour pressure.*

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 or other total pressure. If salt is dissolved in 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.

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°

The **molecular elevation of boiling point,** E, is constant for a given solvent. It is the rise in boiling point for 1 mol of non-volatile solute in 1 kgm. of solvent.

If w gm. of substance in 1000 gm. of solvent raise the boiling point by $D°$, we shall have $D \,.\, E = w \,.\, M$, where M is the molecular weight of the dissolved substance. Hence $M = \frac{Ew}{D}$ (*cf.* the freezing-point equation . $M = \Delta w/D$).

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
Methyl alcohol -	64·7	0·88
Ethyl alcohol -	78·3	1 15
Ether - -	35·4	2 10
Benzene - -	80·2	2 57
Chloroform - -	61·2	3 66

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,

$$E = \frac{RT^2}{1000 L_e}.$$

For water : $T = 100 + 273 = 373$; $L_e = 539$,

$\therefore\ E = 1\ 988 \times (373)^2 - (539 \times 1000) = 0{\cdot}513$ (obs 0·516)

The equations do not hold for concentrated solutions, and the molecular weights are abnormal in solutions of electrolytes

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°.

$w = 2\ 0579 \times 1000/30\ 14 = 68{\cdot}27$, $D = 0{\cdot}566°$, $E = 2\ 10°$;

$\therefore\ M = Ew/D = 2\ 10 \times 68{\cdot}27/0\ 566 = 253{\cdot}3$ But $I_2 = 2 \times 126{\cdot}9 = 253{\cdot}8$;

$\therefore$ 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. 139. The thermometer and the tube for holding the solution are the same as those used in the freezing-point apparatus 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 solvent vapour is condensed in a reflux condenser formed of a limb of the tube, as shown, and the liquid flows back. The boiling point of a weighed amount of the pure

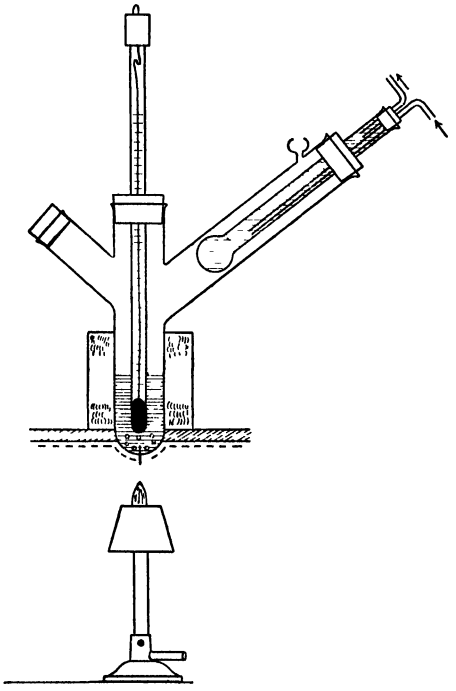


FIG 139 —Beckmann's apparatus for determination of elevation of boiling point.

solvent is first found on the Beckmann thermometer, the mercury column having been suitably adjusted. The tube is then cooled, a weighed quantity of the substance the molecular weight of which is to be found is introduced through the side tube and completely dissolved, and the boiling point of the solution is found The difference is D, the 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 vapour condenses, giving out heat and raises the temperature of the solution until the boiling point is reached The vapour then passes through without condensation. The glass tube A (Fig. 140) contains the solvent, and is heated in the same way as in the preceding apparatus. Inside is the tube B, graduated in c c , containing the solvent and the thermometer Vapour from A bubbles through the solvent by way of the tube C, open to 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. When the solvent in B boils the temperature is read off. The flame is then removed, a weighed quantity of the substance introduced through the side arm, and the heating repeated until the solution boils. The temperature and volume of the boiling solution are read off. The molecular weight is calculated from the formula :

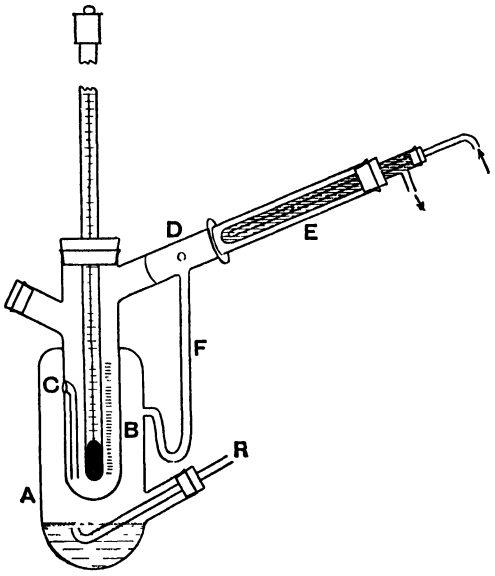


FIG 140 —Landsberger-Beckmann boiling-point apparatus

$$M = K\frac{w}{Ev},$$

where w = weight of solute, v = vol. of solution in c.c., E = observed elevation of boiling point, K = a constant. The values of K for some

common solvents are: water, 540; alcohol, 1560; acetone, 2200; ether, 3030; benzene, 3280.

Deliquescence.—A beaker containing pure water and one containing a solution are placed side by side under a receiver (Fig. 141) Each liquid emits aqueous vapour into the space. If the vapour pressures were the same, equilibrium would be established But the vapour pressure of the water is higher than that of the solution, hence it tends to saturate the space with vapour under a higher pressure than can remain in equilibrium with the solution. Vapour condenses on the latter, and the water is transferred to the solution by **isothermal distillation.** Equilibrium is reached when *all* the pure water is evaporated and absorbed by the solution.

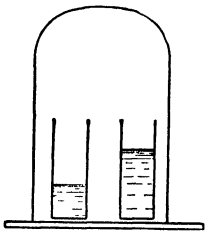


FIG 141 —Isothermal distillation

Many solid salts, such as potassium carbonate and calcium chloride, become damp on exposure to moist air, and in time liquefy completely This is called deliquescence. All deliquescent substances are very soluble in water. In moist air, a little saturated solution is formed Since this is very concentrated, its vapour pressure is less than the partial pressure of aqueous vapour in the atmosphere. Moisture is attracted by the salt, which gradually liquefies to a saturated solution The latter 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.**

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 (ions) gradually *diffuse* upwards until the solution becomes homogeneous and of uniform colour. The dissolved molecules behave to some extent like a gas; they are in motion and possess kinetic energy. If we could interpose a partition in the solution which would stop the dissolved molecules but would be freely permeable to pure water above, we should expect the copper sulphate molecules to exert a bombardment on the partition. A partition freely permeable to pure solvent but 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 filter. Just as ordinary filter-paper will stop suspended particles and

permit dissolved molecules to pass through, the semipermeable membrane may be regarded as stopping even dissolved molecules and permitting only the molecules of pure solvent to pass. 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 pressure to the solution enclosed in it. At lower pressures no solvent percolates through the partition.

Various substances function as semipermeable membranes Without exception they are slimy, non-crystalline bodies, called **colloids.** Thus, if a drop of copper sulphate solution is introduced from a pipette into a solution of potassium ferrocyanide, a skin forms over it, composed of copper ferrocyanide, $Cu_2FeC_6N_6$ This 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 no copper salt diffuses through the drop, as may be seen from the ferrocyanide solution remaining clear The drop expands or shrinks on standing, owing to passage of *water* 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

EXPT 1 —In 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"; Glauber, 1648.)

Measurement of osmotic pressure.—In order to give strength to the copper ferrocyanide membrane, so as to make it capable of withstanding considerable pressures, Pfeffer in 1877 deposited it in the walls of an unglazed earthenware cell, such as is used for the porous pots in galvanic batteries.

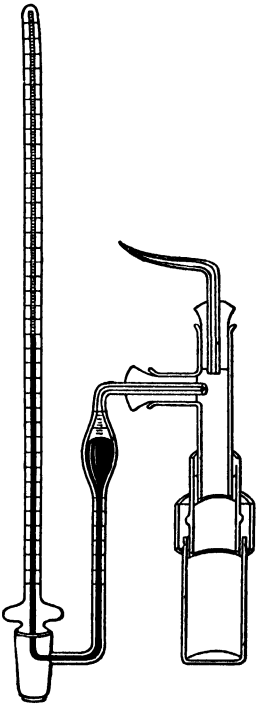


FIG. 142.—Pfeffer's apparatus for measurement of osmotic pressures

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 142. 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 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 said to be obtained by driving the ions, Cu and $FeCy_6''''$, by electrolysis into the pot

The laws of osmotic pressure.—The osmotic pressures of solutions of moderate concentrations are very considerable and have been measured up to 131 atm

The following results were obtained by Pfeffer (1877) with dilute solutions of cane-sugar

OSMOTIC PRESSURES OF SUGAR SOLUTIONS AT 0° C

Concentration, C -	10 03	20 14	40 60	61·38 gm /lit soln.
Pressure, P - -	0 686	1 34	2 75	4 04 atm
Ratio, P/C - -	0 068	0 067	0·068	0 066

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.

OSMOTIC PRESSURES OF 1 PER CENT. CANE-SUGAR SOLUTIONS.

Absolute temp, $T°$	273	279 8	286 7	287·2	288·5	295 0	305 0	309 0
Pressure, P (atm)	0 648	0 664	0 691	0·671	0·684	0·721	0·716	0·746
Ratio P/T 10^3 -	2·38	2·37	2·41	2·33	2 37	2·44	2 35	2·41

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.

The mean value of P/C at 0° C is 0·066 ; this is the osmotic pressure in atm. exerted by 1 *gram* of sugar in 1 litre of solution. Since the molecular weight of sugar is 342, this is also the pressure exerted by 1 *gram molecule* of sugar in 342 litres. The pressure is proportional to the concentration, hence the pressure becomes 1 atm. when the volume containing 1 gram molecule (mol) is $342 \times 0{\cdot}066 = 22{\cdot}6$ litres.

If 1 mol of ideal gas is confined in a space of 22·4 litres at 0° it will exert a pressure of 1 atm. The value 22·6 for a molar solution is

nearly equal to 22·4, hence solutions obey **Avogadro's law.** Van't Hoff in 1886 summarised these results in the statement that *dissolved substances obey the gas laws. The osmotic pressure of a solution is*

VAN'T HOFF.

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. This is known as **van't Hoff's gaseous theory of solution ;** accurate experiments show that it is only approximate, but becomes more exact in the limiting case of extreme dilution, just as the gas laws are exact only at 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 science and especially in its applications to biology.

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 showed, 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. His calculation met with some opposition and gradually dropped out of sight, until it was revived on the basis of the fascinating researches of Jean Perrin, professor at the Sorbonne

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 performing little excursions in an apparently erratic manner and moving in a zigzag path This motion was first observed with suspensions in grains of pollen 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 by C Wiener in 1863 to bombardment of the suspended particles by the molecules of the liquid. 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 Smoluchowski (1906)

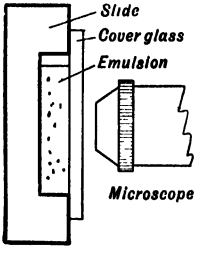


FIG 143 —Perrin's experiment with gamboge emulsion

Perrin found that in a gamboge emulsion examined by the microscope there was a gradation in the density of distribution of the particles with height. Near the surface, a rise of 1/20 mm. halved the number of gamboge particles. This is analogous to the diminution in density of the atmosphere, but 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 gaseous molecules are equally supported against the action of gravity by their kinetic energies. By counting the numbers of particles (Fig. 143) it was possible to find the law of distribution at different heights.

If n and n' are the numbers of gamboge particles per cm.^{3} 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, is connected with the height h by the well-known logarithmic barometric pressure formula. 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 $5 \times 16/22 = 3{\cdot}64$ km. The "molecular weight" of the gamboge particles could thus be calculated from the height in which the number per cm^3 is halved. The weight of each particle was found by counting the number per cm.^{3}, and finding the total weight per cm.^{3} The number of particles required to make up the molecular weight could thus be found · it was $N_0 = 6{\cdot}8 \times 10^{23}$, which is nearly the same as the value of **Avogadro's constant** for a gas By examining the Brownian movement of the suspended particles in tobacco-smoke, de Broglie found $N_0 = 6{\cdot}43 \times 10^{23}$.

The suspended particles in a gamboge emulsion obey the gas laws. It seems very probable that particles in true solutions, 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 solute molecules in a given space is much larger and the pressure is correspondingly greater

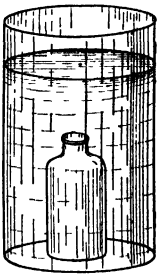


FIG 144.—Graham's experiment on liquid diffusion.

Liquid diffusion.—Liquid diffusion, mentioned previously 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.

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 *kolla*, 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	160	85
Alcohol	200	47
Glucose	300	36
Gum arabic	700	0·8
Albumin	2100	0·3

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. 145), was placed. Crystalloids passed readily through the colloidal septum, whereas colloids were either arrested or diffused exceedingly slowly

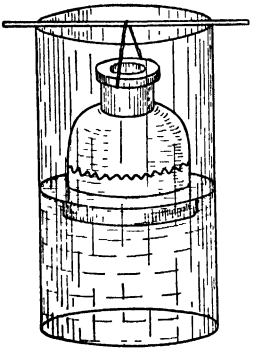


FIG 145 —Graham's dialyser

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 bent into a U-shape, filled with the solution, and placed in a jar through which passes a slow stream of water (Fig 146) 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 are still more efficient

EXPT 2.—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

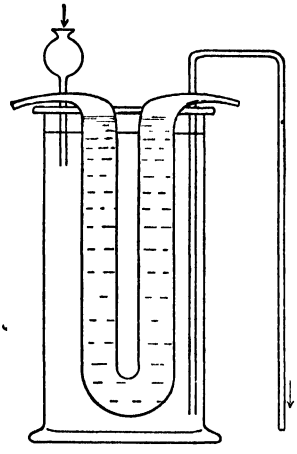


FIG 146 —Tubular dialyser

The colloidal state.—All 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 (ultramicroscopically 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 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; 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, 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.

The idea that colloidal particles are necessarily amorphous is incorrect The X-ray examination of many colloids, such as colloidal gold with particles $1{\cdot}86 \times 10^{-7}$ cm. diameter, colloidal silicic acid, iron oxide, cellulose, gelatin, etc, shows that they contain very small crystals of the substances. Colloidal solutions are generally called **sols**, and the solid forms, which are frequently gelatinous, are called **gels**. A distinction was made between **suspensoids**, in which the colloid particles are solid, and **emulsoids**, in which they are liquid

There are occasional exceptions to this description of the dispersed phase, and a more recent classification is into **lyophobic** (solvent-repelling) and **lyophilic** (solvent-attracting) **colloids**, respectively Lyophobic colloids (*e g*, arsenious sulphide, ferric oxide, gold) are readily precipitated by electrolytes and have viscosities differing only slightly from that of the solvent; lyophilic colloids (gelatin, albumin) are not easily precipitated by electrolytes and are much more viscous than the solvent. Cataphoresis (p. 9) shows that colloid particles are often *charged*; they are precipitated by ions of opposite sign, the ion being adsorbed. Ions of higher valency (Al^{+++}) are much more effective than those of lower valency (K^{+}). A positively charged sol (ferric oxide) and a negatively charged sol (arsenious sulphide) mutually precipitate each other on mixing.

Molecular weights of colloids.—Organic colloids must have high molecular weights; thus, gum arabic, although possessing the empirical formula $C_{12}H_{22}O_{11}$, is acidic, and the very small amount of base required for its neutralisation shows that its molecule is much more complex: $(C_{12}H_{22}O_{11})_7$. By the method of *depression of freezing point* applied to colloidal solutions, high molecular weights have also been found: starch, 25,000; tannin, 1100; silicic acid, 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	$[(C_{12}H_{22}O_{11})_7 = 2394]$

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), 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 generally 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; Sorensen found 34,000 by the osmotic pressure method, and this value was confirmed by Svedberg, using a centrifugal sedimentation method. Svedberg found 375,000 as the molecular weight of casein. The satisfactory agreement between modern results obtained by different methods seems to indicate that colloids possess definite molecular weights, which may 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 402); 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 or treble the normal depression, or an even higher multiple in others, the interpretation was not so clear It might 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 higher depressions for some salts, the identity of the values of the gas constant R from measurements of gaseous density and osmotic pressure, and other experimental evidence, tell 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 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** 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 would account for the abnormally large depression of freezing point. The ions produce depression of freezing point 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 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. A little consideration will show, however, that they must be connected. The osmotic pressure is a mechanical measure of the tendency of liquid solvent to mix with a solution and so dilute it. Since the vapour pressure of a solution is lower than that of the pure solvent, the same tendency for solvent to pass over to solution and dilute it is manifested by isothermal distillation. The relation between freezing point lowering and the lowering of vapour pressure has already been explained. In all cases, it is theoretically possible to obtain work by diluting the solution with pure solvent, but of course the two must not simply be allowed to mix. This statement is most evidently true in the case of osmotic pressure, but the difference of vapour pressures could also produce work in a turbine or other suitable engine. 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*. The three methods are interconnected, and *necessarily* give the same results.

Let solution be contained in a tube A (Fig 147), closed at the lower end by a semipermeable membrane in contact with solvent in C In the tube a column of solution *ab* will be supported by the osmotic pressure The apparatus is enclosed in a vessel B, which contains only the vapour of the solvent The vapour pressure is greater at *a* than at *b* by the weight of the column *ab* of vapour The vapour pressure at *a* is that, f_0, of the pure *solvent* in C, whilst the vapour pressure at *b* is that, *f*, of the *solution* in A Hence $f_0 - f$, the lowering of vapour pressure, increases with the height *ab*, *i e* , with the osmotic pressure, and for small osmotic pressures will be proportional to the latter, *i e* , to the concentration of the solution

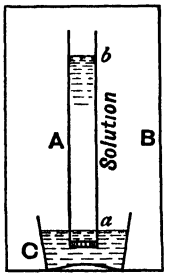


FIG 147 —Osmotic and vapour pressure

The lowering of vapour pressure has been shown to be proportional to the depression of freezing point, hence the latter is proportional to the osmotic pressure, and therefore to the concentration

Let one molecule of electrolyte on *complete* ionisation yield x ions If n gm mols. are dissolved in 1 kgm of water, and if α is the degree of ionisation, the solution will contain $n(1-\alpha)$ gm mols of un-ionised substance and $nx\alpha$ gm mols of ions, or $n[1+(x-1)\alpha]$ gm mols of solute in all If D is the observed depression of freezing point, elevation of boiling point, or osmotic pressure, and Δ the corresponding *normal* value (for $\alpha = 0$), then .

$$D \cdot \Delta = 1 + (x-1)\alpha \cdot 1 ,$$
$$\therefore \alpha = (D-\Delta)/\Delta(x-1),$$

from which (cf. p 126) the value of α may be calculated for a dilute solution

On the other hand, the **conductivity** would, on Arrhenius's theory, be 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 would afford a valuable confirmation of the ionisation hypothesis. The following table shows that there is approximate agreement only.

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

The activity theory of strong electrolytes.—The newer theory of electrolytes puts a different interpretation on these results, since it assumes that in solutions of the concentrations given in the table the ionisations are practically complete, and hence α has not the meaning attributed to it above The variations in conductivity are assumed to be due to changes in *mobility* (p 255) of the ions owing to the electrical forces exerted upon each ion by other ions of opposite sign. The changes in osmotic pressure (and therefore of freezing point) are also regarded as due to the varying attractions exerted between the ions, which at higher concentrations cause the osmotic pressure to have too small a value in the same way as the attractions between gas molecules at higher pressures cause a diminution of pressure on the walls of the vessel On the new theory, the osmotic coefficient $(D-\Delta)/\Delta(x-1)$, and the conductance ratio, Λ/Λ_∞ are not exactly but only approximately equal Just as the change in equivalent conductivity is explained by varying mobility of the ions with concentration, so the variations of the osmotic effect are correlated by changes of **activity** of the ions with concentration, the number of ions remaining the same in both cases.

Let P_i be the osmotic pressure calculated on the assumption that the electrolyte is *completely ionised* and obeys the gas laws, *i e*, for a binary electrolyte $P_i = 2cRT$ On account of the interionic attraction the observed osmotic pressure P is less than P_i, but becomes equal to it at infinite dilution Let

$$\frac{P_i - P}{P_i} = 1 - f_0 = \theta, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where f_0 is the **osmotic coefficient,** which becomes 1 in very dilute solution, when θ vanishes Equation (1) holds with D_i and D, or E_i and E, the ideal and observed depressions of freezing point, or elevations of boiling point, on the assumption of *complete ionisation*, as well as with P_i and P, since these are proportional, quite independently of any theory of solutions

The value of θ, therefore, represents the deviation from the ideal gas laws exhibited by the ions in solution The theory of Debye and Huckel shows that for an electrolyte giving two ions of unit charge $(B^+ + A^-)$, at a *total* molar concentration c

$$\theta = 1 - f_0 = \beta\sqrt{c} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Although experiment generally confirms the form $\beta\sqrt{c}$, the value of the constant β calculated from theory does not always agree with experiment

It is convenient to introduce another coefficient, called the **activity coefficient,** f, defined as

$$f = \frac{a}{c}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

a being the **activity** of the dissolved substance, as explained in Chapter XX Then the Debye-Huckel theory leads to the relation, for an electrolyte of the type considered :

$$-\log_e f = 3\beta\sqrt{c}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where $\log_e$ is the natural logarithm, equal to 2·3026 times the logarithm to the base 10 Here again, experiment confirms approximately the relation with $\sqrt{c}$, but not always the theoretical value of β

We must remember that the simple interpretation of Λ/Λ_∞, the conductivity ratio, as giving the degree of ionisation α, no longer holds in the new theory, nor does the relation of this to the osmotic pressure etc take the form previously deduced Instead we must introduce a new **conductivity coefficient**:

$$\frac{\Lambda}{\Lambda_\infty}=f_c \quad \ldots\ldots\ldots\

from one molecule of electrolyte, and α is the **degree of ionisation.** On this theory, the same value of α should be obtained from the conductivity ratio, Λ/Λ_∞. On the new theory of **strong electrolytes,** these are practically completely ionised at all concentrations in dilute solutions ($< 0{\cdot}01N$), and the variations of osmotic pressure etc., and of Λ, are referred to interionic attraction. The value α then has no meaning and is replaced by **osmotic** and **conductivity coefficients,** f_0 and f_c (not to be confused with the vapour pressures). Arrhenius's theory, however, is very nearly true for a **weak electrolyte,** since then the interionic attractions are weak and the electrolyte is only partly ionised.

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 Schonbein, 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 1.—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 10^7. 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 contained in electrolytic oxygen and in the oxygen evolved by the action of fluorine on water, or by the action of concentrated sulphuric acid on barium peroxide It is produced by heating crystalline periodic acid, by passing oxygen over heated manganese dioxide, by the action of radium salts on oxygen, and by heating ammonium persulphate with nitric acid.

EXPT 2.—Stir a little barium peroxide with concentrated sulphuric acid. The smell of ozone is perceptible.

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 supposed to be formed by the slow combustion of ether vapour on glowing platinum wire, but the substance produced is probably hydrogen peroxide. 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 This gas does not contain oxides of nitrogen. Liquid oxygen exposed to ultra-violet light becomes dark blue, owing to the production of liquid ozone

In all cases, ozone is obtained mixed with oxygen in varying amounts the product is ozonised oxygen (or ozonised air).

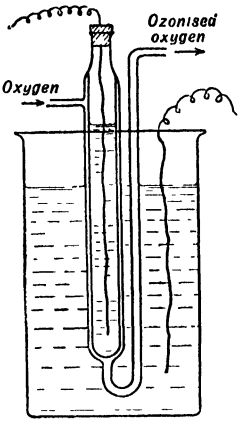


FIG 148 —Brodie's ozoniser.

The preparation of ozone.—The most convenient method of preparing ozonised oxygen is by the action of a silent electric discharge on oxygen, preferably dry. Many types of apparatus are used, all very similar in principle One of the simplest (Fig 148) is that of Brodie (1872).

EXPT. 3.—The oxygen passes slowly through the annular space between two glass tubes, the inner tube filled with dilute copper sulphate solution, and the whole apparatus placed in a jar of the same liquid The wires from a coil dip into the liquids, which form electrodes and at the same time serve to cool the apparatus A bluish-violet glow is seen

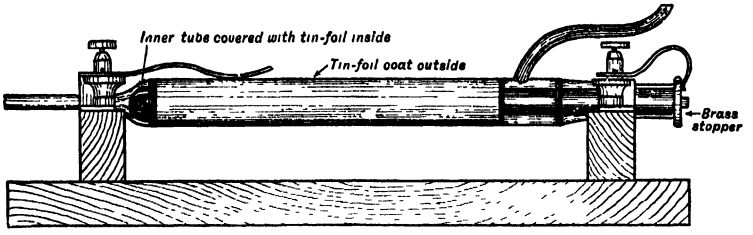


FIG. 149 —Siemens' ozoniser

in the glass surfaces, usually 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 ordinary corks or paraffin wax. Rubber is quickly destroyed by ozone, dry cork is more resistant. Air may be used instead of oxygen, but less ozone is obtained, and oxides of nitrogen may be formed.

The original ozoniser of Siemens (1858) consists (Fig. 149) of two

concentric glass tubes, the outer covered, and the inner lined, with tinfoil, but Brodie's is superior in many ways By cooling the whole apparatus at 0°, using a powerful coil, and avoiding sparks, as much as 25 per cent by weight of the oxygen may be converted into ozone; usually the yield is less.

It was formerly assumed that the formation of ozone from oxygen is due to a splitting up of the oxygen molecules into atoms, which then react with O_2 molecules to form O_3. Warburg found that ultraviolet light of wave-length 209 $m\mu$ produces ozone, and since the line 185 $m\mu$ is the only one from the mercury lamp strongly absorbed by oxygen it is probably the chemically active one, corresponding (p. 199) with the energy 165 k cal This could dissociate the O_2 molecule into normal atoms (118 k cal), but it is supposed (Mecke, 1931) that the first product is an excited oxygen molecule $O_2 + h\nu = O_2''$, which dissociates an O_2 molecule into atoms, at the same time forming a metastable O_2' molecule with no surplus energy: $O_2'' + O_2 = O_2' + 2O$, followed by $O + O_2 = O_3 + 27$ k cal. Warburg found that two molecules of ozone are formed per absorbed quantum

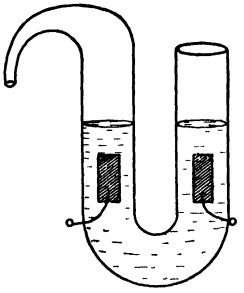


FIG 150 —Ozone from sulphuric acid by electrolysis

EXPT 4.—Ozonised oxygen is formed by the electrolysis of sulphuric acid (sp gr 1·1) The apparatus is shown in Fig 150. 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°

The composition of ozone.—Schonbein found that ozonised oxygen passed through a glass tube heated to 400°, loses its smell and action on potassium iodide, and the gas then appears to be ordinary oxygen.

EXPT 5 —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 On allowing the tube to cool the reaction appears again

Marignac and de la Rive (1845) and Shenstone and Cundall (1887), found that pure dry oxygen can be ozonised by an electric discharge. Briner and Durand (1907) converted a confined volume of oxygen completely into a blue liquid mixture of ozone and oxygen 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. 151), *A* containing potassium iodide

solution, and *B* concentrated sulphuric acid. The increase in weight of the two bulbs was exactly equal to the oxygen equivalent ($O = I_2$) of

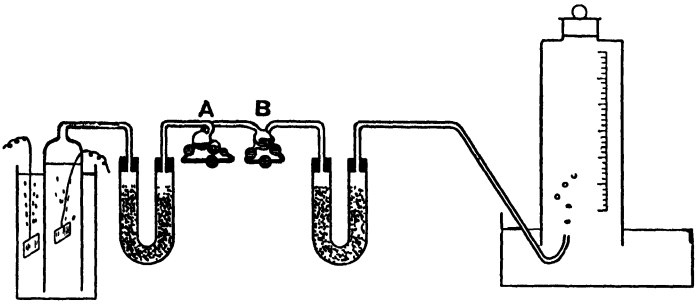


FIG 151 —Andrews' experiments on ozone

the iodine liberated The bulb *A* was then replaced by a glass tube heated to 400°. The weight of the bulb *B* 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.

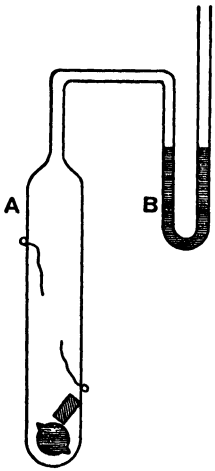


FIG. 152.—Andrews and Tait's experiments on ozone

The formula of ozone.—Andrews and Tait (1860) filled a tube, *A* (Fig. 152), with dry oxygen, which communicated with a sulphuric acid manometer, *B*. Sulphuric acid is without action on ozone After the silent discharge, 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 a variable volume of gas remained. A bulb of potassium iodide solution broken in the gas produced iodine, and the volume of gas remained unchanged, although it no longer expanded after heating to 300° and was therefore completely converted into oxygen.

A possible explanation of the constancy of volume of the gas when the ozone is destroyed by potassium iodide 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:

$$2KI + O_3\ (1\ vol) + H_2O = 2KOH + O_2\ (1\ vol.) + I_2.$$

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 1866–68 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 formulae 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 with the following formulae

O_3		O_4		O_{22}	
$70O_2$	$70O_2$	$80O_2$	$80O_2$	$89O_2$	$89O_2$
$20O_3$	$30O_2$	$10O_4$	$20O_2$	O_{22}	$11O_2$
90	100	90	100	90	100

In order to find the relative volume of ozone in the mixture, some solvent or absorbent is 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 (or contraction on ozonisation) it would be possible to distinguish among the above cases. Thus, if the formula is O_3, the contraction on absorption is 20, the expansion on heating $100 - 90 = 10$ If the formula is O_4, the contraction is 10 and the expansion 10; if the formula is O_{22}, the contraction is 1 and the expansion 10 *The formula O_3 thus requires that the contraction on absorption shall be double the expansion on heating.*

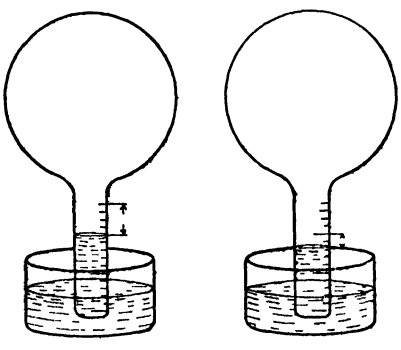


FIG 153 —Soret's first experiments on ozone

Soret found that suitable absorbents for ozone were certain essential oils, such as oil of cinnamon and oil of turpentine. He took two flasks,

* "*Eau oxygénée et ozone,*" in *Classiques de la Science* (III), pub. A. Colin, Paris, 1913.

of 250 c.c. capacity, filled with ozonised oxygen (Fig. 153). 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.

EXPT. 6.—The apparatus shown in Fig. 154, devised by Newth (1896), consists of two concentric glass tubes, the inner fitted into the outer by a ground-glass joint. The inner tube contains dilute sulphuric acid, and the apparatus, previously filled with dry oxygen, is supported in a jar of water and crushed ice Two wires from the coil dip into the liquids By means of projections from the inner and outer tubes a thin glass tube, *a*, containing oil of turpentine or oil of cinnamon is held in position in the annular space The manometer containing concentrated sulphuric acid coloured with indigo communicates with the apparatus, and the oxygen is ozonised The contraction 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 twice the contraction on ozonisation, *i.e.*, double the expansion which would have occurred on decomposing the ozone by heat In each case, before reading off the volume, an adequate time must be allowed for the gas to assume a constant temperature.

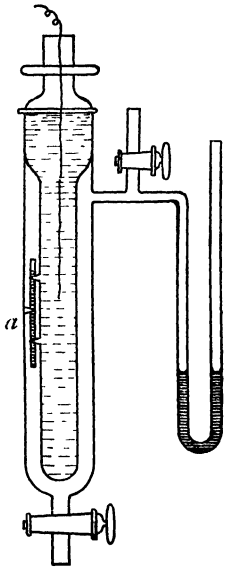


FIG 154.—Absorption of ozone by turpentine

The density of ozone.—Soret, in a second research (1868), made use of Graham's law of diffusion. If ozone has the formula O_3 (density 24) it should diffuse rather more slowly than carbon dioxide, but more rapidly than chlorine. The diffusion rates are inversely proportional to the square roots of the densities:

$$\frac{\text{Rate of diffusion of } CO_2}{\text{Rate of diffusion of } O_3} = \frac{\sqrt{24}}{\sqrt{22}}; \quad \frac{\text{Rate of diffusion of } Cl_2}{\text{Rate of diffusion of } O_3} = \frac{\sqrt{24}}{\sqrt{35{\cdot}5}}.$$

In order to get over the difficulty of the dilution of ozone with oxygen, Soret allowed the gases to diffuse into pure oxygen and 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.

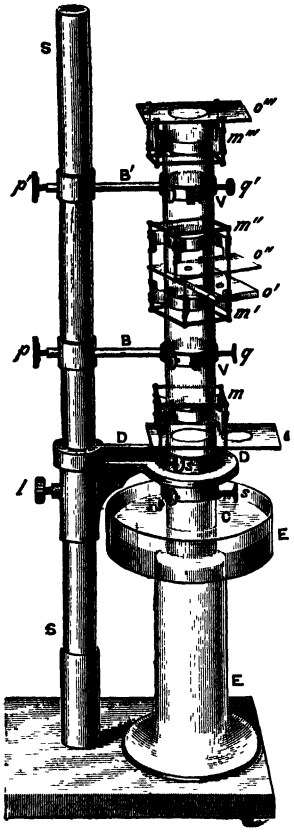


FIG 155.—Density of ozone by diffusion (Soret)

The apparatus (Fig 155) consisted of three glass tubes, B, B', and C, placed over sulphuric acid in E, and separated by sliding glass plates with holes, 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, 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 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 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 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 $\sqrt{24/35\cdot5} = 0\cdot822$. 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 $\sqrt{22/24} = 0\ 95$. The agreement is to 3 per cent, which is satisfactory, as the ozonised oxygen contained only 5 per cent. of ozone by volume

In 1898 Ladenburg obtained nearly pure ozone by the evaporation of the liquid and compared the times of effusion of equal volumes of this gas and of oxygen in a Bunsen's effusion apparatus, he found 430

secs and 367·4 secs, respectively The squares of the times of equal effusion are proportional to the densities, hence 430^2 $367{\cdot}4^2 = x$ 16, or $x = 22$ Since the gas contained a little oxygen, which would make the density lower, this result is sufficiently near the value 24 to confirm the formula O_3.

The formula O_3 for ozone was completely established by a determination of the vapour density of *pure* ozone by Dumas' method. The value 24 was found (Riesenfeld, 1922). All other formulae were shown to be excluded

Ozone is an allotropic modification of oxygen The cause of allotropy lies in the different molecular complexities the molecule of ordinary oxygen, O_2, contains two atoms, whilst ozone contains three atoms of oxygen in the molecule, O_3 Ozone is 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 than the oxygen from which it is produced: it is an endothermic substance: $3O_2 = 2O_3 - 2 \times 34$ k. cal. Like other endothermic substances, it is stable at high temperatures If oxygen is strongly heated, some ozone is produced· $3O_2 \rightleftharpoons 2O_3$ 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 is arrested. Ozone is produced in hydrogen or acetylene flames, or when a platinum wire or Nernst filament is strongly heated by an electric current under liquid oxygen Ozone is produced when a hydrogen or carbon monoxide flame impinges on liquid oxygen.

The properties of ozone.—Ozonised oxygen usually does not contain more than 15 per cent by volume of ozone. If cooled by passing through a tube immersed in liquid oxygen, a deep-blue liquid separates. On reducing the pressure, evaporation takes place, and the liquid separates into an upper, deep blue layer, which is a solution of ozone in liquid oxygen, and a lower, violet-black layer, which is a solution of oxygen in liquid ozone. The oxygen may be pumped off from the strongly cooled lower layer, and pure **liquid ozone,** b. pt $-112{\cdot}4°$, obtained. On careful evaporation this gives a deep-blue gas, containing 100 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 fairly stable in the absence of catalysts, but explodes if heated or brought in contact with organic matter. On cooling the liquid in liquid hydrogen, violet-black crystals of **solid ozone,** m. pt $-249{\cdot}7°$, are formed. The critical temperature of ozone is $-5°$.

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 slightly accelerates the decomposition: reduced pressure, chlorine, oxides of nitrogen, and phosphorus pentoxide, rapidly accelerate it

Ozone is more soluble than oxygen in water · 1 vol of water at 0° dissolves 0·49 vols of ozone 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 On shaking with water, the mercury recovers its original form. This reaction is due to oxidation to Hg_2O, which dissolves in mercury (H B Baker)

Ozone is catalytically decomposed in contact with metallic silver, platinum, and palladium, and with oxides of manganese, cobalt, iron, lead, and silver, and by shaking it with powdered glass In the case of silver the metal, if warm, is blackened and an oxide is probably alternately formed and reduced:

$$2Ag + O_3 = Ag_2O + O_2\,; \quad Ag_2O + O_3 = 2Ag + 2O_2.$$

Barium and hydrogen peroxides react with ozone: $BaO \cdot \boxed{\overline{O+O}} \cdot O_2 = BaO + 2O_2$, 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; another is $3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O$.

Ozone, containing more energy than oxygen, 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 · (1) $2HCl + O_3 = Cl_2 + H_2O + O_2$; (2) $10HI + 4O_3 = 5I_2 + 4H_2O + H_2O_2 + 3O_2$ (acidified potassium iodide solution). Ammonia is oxidised to ammonium nitrite and nitrate; a solution of potassium ferrocyanide is oxidised to ferricyanide:

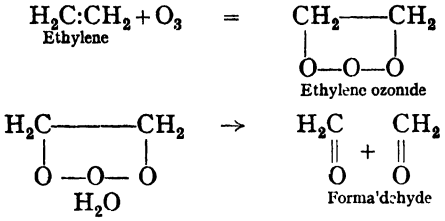
$$2K_4FeC_6N_6 + H_2O + O_3 = 2K_3FeC_6N_6 + 2KOH + O_2.$$

The liberation of iodine from potassium iodide constitutes a test for ozone, although iodine is liberated by other oxidising agents (*e.g.*, H_2O_2, chlorine and bromine, and higher oxides of nitrogen). The reaction: $O_3 + 2KI + H_2O = O_2 + I_2 + 2KOH$, occurs in a neutral solution, which then becomes alkaline. In presence of alkali, the iodine is partly converted into iodide and iodate, but is wholly liberated again on acidifying:

$$3I_2 + 6KOH = 5KI + \dot{K}IO_3 + 3H_2O\,;$$
$$5KI + KIO_3 + 3H_2SO_4 = 3K_2SO_4 + 3I_2 + 3H_2O.$$

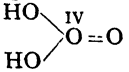
Moist iodine is oxidised to iodic acid, HIO_3: $I_2 + 5O_3 + H_2O = 2HIO_3 + 5O_2$. Dry iodine is converted into a yellow powder, supposed to be I_4O_9, without change of volume of the gas: $2I_2 + 9O_3 = I_4O_9 + 9O_2$. An alkaline solution of potassium iodide is oxidised to iodate (KIO_3), and periodate (KIO_4).

Carbon compounds containing double linkages 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 one 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. $O{=}\overset{IV}{O}{=}O$, but the simpler formula is more probable; it also agrees with the formula of hydrogen peroxide.

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 was regarded by Baeyer and Villiger as **potassium ozonate**, but on acidification it does not give ozone but oxygen and 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 halogens, 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 Paper soaked in a solution of potassium iodide and starch is, therefore, of little value in the detection of ozone in air, since the preceding substances may be present. The lower oxides of nitrogen cannot exist simultaneously with excess of ozone, but are at once oxidised to the pentoxide, N_2O_5.

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 and the equivalent amount of ozone ($O_3 = I_2$) calculated. Another method of estimation depends on the oxidation of sodium nitrite solution:

$$NaNO_2 + O_3 = NaNO_3 + O_2.$$

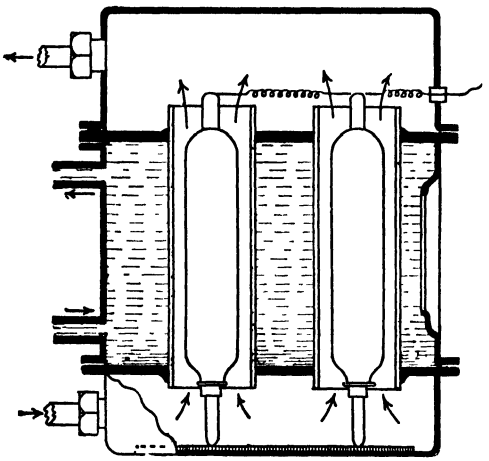


FIG. 156 —Siemens and Halske ozoniser

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 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.

Technical utilisation of ozone.—Air or oxygen is ozonised on the technical scale by the silent electric discharge. The **Siemens and Halske ozoniser** (Fig. 156) consists of a battery of glass or porcelain tubes with internal tubes of aluminium, enclosed in an earthed iron tank of water 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 insulator, 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,

at a concentration of 2 gm. of ozone per cu. m. of air. With pure oxygen, 120–180 gm. are obtained. The yields are 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); also for purifying air (*e g*, in underground railways) and for oxidation processes (*e g*, *iso*-eugenol to vanillin). 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.

CHAPTER XIX

HYDROGEN PEROXIDE

Hydrogen peroxide.—Barium monoxide or baryta, BaO, can absorb oxygen, forming a higher oxide, BaO_2, called **barium peroxide,** which is produced . (*a*) by passing a stream of oxygen over baryta heated to dull redness . $2BaO + O_2 \rightleftharpoons 2BaO_2$; (*b*) by adding baryta to fused potassium chlorate, and washing out the soluble potassium chloride from the residue with water : $3BaO + KClO_3 = 3BaO_2 + KCl$.

If barium peroxide is added to cold dilute hydrochloric acid, no oxygen is evolved ; the solution contains a new substance, hydrogen peroxide $BaO_2 + 2HCl = BaCl_2 + H_2O_2$, which Thenard, its discoverer (1818), called *oxygenated water.*

It is 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 hydrogen peroxide free from soluble salts, barium peroxide may be treated with an acid, such as sulphuric, carbonic, phosphoric or hydrofluosilicic (H_2SiF_6), which forms an insoluble barium salt. The filtrate is an aqueous solution of hydrogen peroxide.

Expt. 1 —Stir barium peroxide with distilled water 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 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 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 acid, on account of the formation of a coating of insoluble sulphate on the particles of peroxide. A *hydrated* barium peroxide, $BaO_2,8H_2O$, is readily decomposed by this acid, and is prepared as follows. Commercial barium peroxide 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 iron and aluminium impurities as hydroxides. These, together with the silica originally contained in the barium peroxide, are filtered off, and the filtrate is added to 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 :

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2 ;$$
$$H_2O_2 + Ba(OH)_2 + 6H_2O = BaO_2,8H_2O.$$

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 :

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2 ;$$
$$BaO_2 + H_2SiF_6 = BaSiF_6 + H_2O_2$$

Barium peroxide also hydrates slowly when stirred with water and can then be decomposed by adding phosphoric acid, followed by sulphuric acid This method is used on the large scale.

Metallic sodium burns in oxygen with a yellow flame, and a yellow mass of **sodium peroxide**, Na_2O_2, is left.

EXPT. 2 —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 manufactured by heating sodium in a current of dry air, purified from carbon dioxide. The calculated amount 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 separate as crystals of Glauber's salt, $Na_2SO_4,10H_2O$, and the liquid is then decanted and distilled *in vacuo*. 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*

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 30 per cent. preparation evolves 100 volumes of oxygen. From the equation 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

329·4 c.c. of O_2. A 1 per cent. solution evolves 3·294 times its volume of oxygen; "10 vol." peroxide is 3·04 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 enriched in peroxide. It may 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 exhausted desiccator containing concentrated sulphuric acid. When a certain concentration of peroxide is reached, the latter begins to volatilise, but by working at low temperatures Thenard was able to obtain a liquid (sp gr 1·452) giving off 475 vols. of O_2 at 14°, *i e*, containing 95 per cent. of H_2O_2

These concentrated solutions easily decompose on heating, or even at the ordinary temperature. They are rendered more stable by a trace of acid. Dilute aqueous solutions are stable if acidified.

More concentrated hydrogen peroxide may be obtained by distillation under reduced pressure; this method was also used by Thenard.

Pure hydrogen peroxide.—In 1894 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 is 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°, it is concentrated to 66·6 per cent. Some peroxide was lost, not by decomposition, but by evaporation, since it is 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 was then distilled at a pressure of 65 mm; the fraction coming over between 81° and 85° contained 90·5 per cent. of H_2O_2. This was again fractionated under reduced pressure, and the fraction between 84° and 85° contained 99·1 per cent. of H_2O_2, and was free from all impurities.

The apparatus used for distillation under reduced pressure consists (Fig. 157) of a distilling flask, containing the solution of hydrogen peroxide, fitted with a thermometer, and placed on a water-bath. The side tube 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 connnected with a good water pump. 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 experiment there is some danger of explosion, when the apparatus is shattered. This appears to be due to the formation of unstable ethyl hydroperoxide, $C_2H_5HO_2$, discovered by Brodie, which is produced from the ether remaining in the peroxide It is safer to begin the experiment directly with Merck's 30 per cent perhydrol, which has not been treated with ether

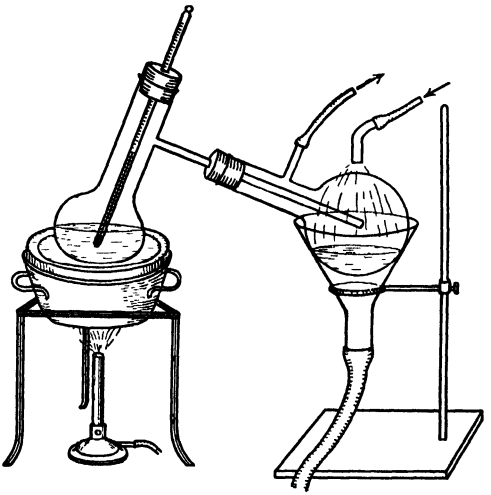


Fig 157.—Distillation under reduced pressure.

Properties of pure hydrogen peroxide. — 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. When heated to 151°, the boiling point at 760 mm , the substance explodes violently. Its specific gravity is 1·4649 at 0°. The liquid has a strong *acid* reaction to litmus. In dilute solution hydrogen peroxide is completely neutral. 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 −1·70°, are obtained. These crystals explode with a trace of platinum black ; alone, they are fairly stable. By mixing the pure peroxide with water and cooling in a mixture of solid carbon dioxide and ether, the crystalline hydrate . $H_2O_2,2H_2O$, m. pt. −51°, is obtained.

The stability of hydrogen peroxide.—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; the commercial peroxide, but not Merck's perhydrol, is acid The addition of alcohol, glycerin, or barbituric acid also renders the solutions stable. The vapour appears to be stable

Hydrogen peroxide closely resembles ozone in many respects Although it is an exothermic compound when formed from the elements $H_2 + O_2 = H_2O_2 + 45{\cdot}2$ k. cal, hydrogen peroxide readily decomposes into gaseous oxygen and water, and is unstable at the ordinary temperature As in the case of ozone, one of the oxygen atoms tends to split off, with the formation of gaseous oxygen and water and this decomposition is attended with a very large evolution of heat:

$$2H_2O_2 = 2H_2O + O_2 + 2 \times 23{\cdot}0 \text{ k cal}$$

Hydrogen peroxide is produced in some combustion reactions. 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

Traces of hydrogen peroxide are formed by passing a mixture of hydrogen and oxygen over palladium-black $H_2 + O_2 = H_2O_2$ 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, $2H_2O + O_2 = 2H_2O_2$, or on a non-explosive mixture of hydrogen and oxygen at $-80°$, or the mixture $H_2 + O_2$ at 3 cm pressure 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 said to be formed in plants

Expt 3.—Allow a hydrogen flame to impinge on a piece of ice. Pour out the liquid produced, and add a little titanic acid solution (p. 302): a yellow colour indicates the presence of hydrogen peroxide

Addition compounds of hydrogen peroxide.—Hydrogen peroxide forms addition 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. The crystalline compound with urea, CON_2H_4,H_2O_2, stabilised by a trace of citric acid, is known commercially as *hyperol*· it liberates hydrogen peroxide when dissolved in water The crystalline compound, $(NH_4)_2SO_4,H_2O_2$, obtained from 30 per cent. hydrogen peroxide and ammonium sulphate, gives very concentrated hydrogen peroxide when distilled in a vacuum.

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 known.

Oxidising reactions 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 utilised in restoring discoloured oil-paintings in which the white-lead pigment (basic lead carbonate) has become converted into black PbS by atmospheric hydrogen sulphide Ferrous salts in acid solution are converted into ferric salts · $2FeSO_4 + H_2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O$. This reaction may be used in the estimation of hydrogen peroxide

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.

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. 4.—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 this "active," and the activated oxygen, probably in the atomic condition, then reacts with the labile oxygen atom of the peroxide: $H_2O \cdot O + O = H_2O + O_2$ Finely divided silver, manganese dioxide, and other substances also cause catalytic decomposition.

Reducing actions of hydrogen peroxide.—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. 5.—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 when hydrogen peroxide acts as a reducing agent, the labile oxygen atom withdraws another oxygen atom from the compound reduced, to produce a molecule of gaseous oxygen. It reacts (rather slowly) with ozone:

$$O_2 \cdot \quad O + O \quad \cdot H_2O = O_2 + O_2 + H_2O.$$

Hydrogen peroxide is used as an *antichlor* to remove excess of chlorine from bleached fabrics: $Cl_2 + H_2O_2 = 2HCl + O_2$.

A solution of potassium permanganate acidified with sulphuric acid is readily reduced by hydrogen peroxide, with evolution of oxygen:

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Manganese dioxide brings about an evolution of oxygen from a *neutral* solution of hydrogen peroxide, the action being apparently catalytic, but in *acid* solution the manganese dioxide is reduced to a manganous salt: $MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2$

Solutions of bleaching powder and sodium hypobromite 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.

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, with evolution of oxygen: $2K_3FeC_6N_6 + 2KOH + H_2O_2 = 2K_4FeC_6N_6 + 2H_2O + O_2$.

Hydrogen peroxide acts powerfully on a photographic plate. The effects of traces of this substance have often been attributed to "rays"

Tests for hydrogen peroxide.—One part of peroxide in 25 million parts of water may be detected by the liberation of iodine from potassium iodide, giving a blue colour with starch Other substances, such as ozone and nitrites, give this reaction. The liberation of iodine occurs somewhat slowly, but is rapid in presence of ferrous sulphate: $2KI + H_2O_2 = 2KOH + I_2$.

The most delicate reaction for hydrogen peroxide is the formation of a yellow colour, 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.

A delicate test is the formation of a deep blue perchromic acid with chromic acid, CrO_3.

EXPT 6.—To very dilute hydrogen peroxide is added a dilute solution of potassium dichromate acidified with sulphuric acid. The solution is rapidly shaken with ether, which floats to the surface with a

beautiful blue colour. An unstable perchromic acid is formed, 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 (1) guaiacol solution acidified with sulphuric acid gives a blue colour ; (2) guaiacum tincture, with a little blood, or malt extract, 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 at 90° is 17 ; the molecular weight of the substance has been found from the freezing point of its aqueous solution (Carrara, 1892) to be 34 ; hence its formula is H_2O_2 In the pure state hydrogen peroxide, like water, is probably associated.

The constitutional formula may be H·O·O·H, *i.e*, **dihydroxyl**, HO·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 suggests that it is linked differently from the other, Kingzett (1884) wrote the formula $O=O\swarrow^{H}$—H, in which one oxygen is quadrivalent. In the modern theory of valency (p 453) the maximum covalency of oxygen is three, and this formula would have to be written as $[O=O-H]^-H^+$, a weak acid. The concentrated peroxide evolves carbon dioxide from a solution of sodium carbonate added to it drop by drop · $H_2O_2 + Na_2CO_3 = Na_2O_2 + H_2O + CO_2$. (If the peroxide is added to the carbonate, pure oxygen is evolved by catalytic decomposition.)

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·OH. This agrees with the formula C_2H_5 O O C_2H_5 :

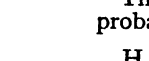
$$C_2H_5\cdot O\cdot O\cdot C_2H_5 = C_2H_5\cdot OH + HO\cdot C_2H_5$$
$$\uparrow\quad\uparrow \qquad\qquad\qquad\qquad\qquad\qquad$$
$$H\quad H$$

Kingzett's formula, on the contrary, would require that ether, $(C_2H_5)_2O$, should be formed :

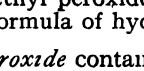
$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O=O\rightarrow \quad \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O + H_2O.$$
$$\uparrow$$
$$2H$$

The formula of ethyl peroxide is therefore $C_2H_5\,O\,O\,C_2H_5$ and it is probable that the formula of hydrogen peroxide is H O·O H.

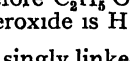
H_2O_2 is a *true peroxide* containing two singly linked oxygen atoms



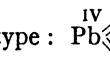
. Sodium peroxide is



and barium peroxide



. True peroxides, which give hydrogen peroxide with dilute acids, differ in constitution from the *dioxides* of lead, manganese, etc, which give oxygen with concentrated sulphuric acid, and chlorine with concentrated hydrochloric acid. Their formulae are of the type:



. This is confirmed by the formation of unstable higher chlorides on treatment with cold concentrated hydrochloric acid, *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 (Brodie, 1863) ·

$$BaO_2 + 4HCl = BaCl_2 + Cl_2 + 2H_2O$$

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 Schonbein in 1858. He found that the oxygen is equally divided in oxidising the substance (*e.g*, lead) and in forming hydrogen peroxide;

$$Pb + O_2 + H_2O = PbO + H_2O_2.$$

Clausius (1858) considered that the oxygen molecule contained a positively and a negatively charged atom of oxygen, 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

Traube (1882) suggested that in oxidation processes in the presence of gaseous oxygen the oxygen molecule unites as a whole with the oxidisable substance to form a **holoxide**, or **moloxide**. For example, in the combustion of hydrogen the latter unites with O_2 to form hydrogen peroxide as a primary product $H_2 + O_2 = H_2O_2$ The reaction between zinc, water and oxygen he represented as

$$Zn + O\ H_2 + O_2 = ZnO + H_2O_2,$$

and the primary oxidation of carbon monoxide as.

$$CO + O\ H_2 + O_2 = CO_2 + H_2O_2.$$

Bach (1897) concluded that the substance undergoing oxidation (**autoxidiser**, *A*) itself unites with a molecule of oxygen to form an unstable higher oxide, which may then react with water or some other **acceptor**, *B*, to give the lower oxide of *A*, and H_2O_2 or BO:

$$A + O_2 = AO_2.$$
$$\begin{cases} AO_2 + H_2O = AO + H_2O_2, \\ AO_2 + B = AO + BO. \end{cases}$$

With metals, the unstable higher oxides PbO_2, ZnO_2, are not the ordinary known ones, which do not give hydrogen peroxide with water.

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 Turpentine forms a peroxide on standing in a loosely stoppered bottle

Expt. 7.—Add a little turpentine to dilute potassium iodide and starch solution in an open flask, shake, and allow to stand. A blue colour is produced.

Induced oxidation.—A solution of sodium arsenite, Na_3AsO_3, is not oxidised to arsenate on exposure to air, but a solution of sodium sulphite, Na_2SO_3, is oxidised to sulphate on exposure When a solution containing both arsenite and sulphite is exposed to air, *both* salts are oxidised .

$$Na_2SO_3 + Na_3AsO_3 + O_2 = Na_2SO_4 + Na_3AsO_4.$$

This induced oxidation may be explained on Clausius's or on Bach's theories. The Na_2SO_3 is called an **inductor,** the O_2 molecule the **actor,** and the Na_3AsO_3 (which is not oxidised by itself) the **acceptor :**

$$\text{I. } Na_2SO_3 + O\ \ O + H_2O = Na_2SO_4 + H_2O_2,$$
$$Na_3AsO_3 + H_2O_2 = Na_2SO_4 + H_2O.$$

$$\text{II. } Na_2SO_3 + O_2 = Na_2SO_5,$$
$$Na_3AsO_3 + Na_2SO_5 = Na_2SO_4 + Na_3AsO_4.$$

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 example, 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) 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 example, 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 AB can never take place [completely], but the body B will be divided between the bodies A and C 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. 148). 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 138) $2BaO_2 \rightleftharpoons 2BaO + O_2$, and the dissociation of steam at high temperatures (p 148) $2H_2O \rightleftharpoons 2H_2 + O_2$ Such reactions as the above, which can proceed in either direction, are called **reversible reactions.**

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, slightly soluble (*cf* p 85) and the reactions proceed *in solution*

EXPT 1.—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) $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$.

Very general statements, to the effect that *all* reactions are really reversible, must be accepted with reserve Many chemical reactions appear to be irreversible under all known conditions 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 in Lavoisier's experiment 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). 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

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. The same state of equilibrium is reached on heating hydrogen iodide at 444° for a sufficient time as 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. 158. *ACD* represents the amounts of hydrogen iodide left after various times when that gas is heated; *BCD* represents the amounts of hydrogen iodide formed from hydrogen and iodine. 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 both are still proceeding, but the amount of hydrogen iodide formed in any instant is exactly equal to the amount decomposed The two reactions are balanced, and a state of **kinetic equilibrium** is attained

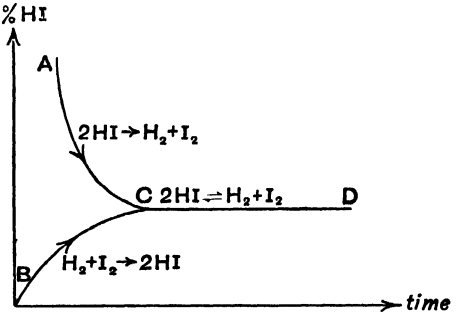


FIG 158.—Curves illustrating attainment of equilibrium state

The conception of equilibrium as the balance of two opposing reactions follows from the kinetic theory A liquid comes into equilibrium with its vapour when as many molecules leave the liquid as return to it in a given interval. 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. Barium peroxide heated in a closed vessel at a constant temperature, 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 oxygen pressure, the more frequent are collisions of oxygen molecules on the baryta and the greater is the rate of recombination. The rate at which the peroxide molecules break 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 oxygen pressure 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**, *v.* p. 138).

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.

When sulphuric acid is poured over common salt, a state of equilibrium is 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 hydrochloric acid gas is expelled by heating, further reaction occurs

When 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) Precipitated barium sulphate is appreciably soluble in concentrated hydrochloric acid.

Investigation of equilibrium states.—The preceding examples show that a state of equilibrium may be disturbed by withdrawing one or more of the interacting substances from the sphere of action. In examining the proportions of substances existing in equilibrium, it must be ensured that the reverse reaction does not take place when the conditions are changed. 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 after *rapidly* cooling the mixture, when very little reaction occurs 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.

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.

Deville (1864) demonstrated the dissociation of gases at high temperatures by means of the apparatus shown in Fig. 159. A wide tube of glazed porcelain, with a narrower tube of unglazed porcelain sup-

ported 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

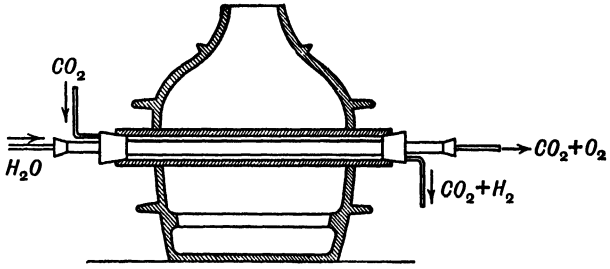


FIG 159 —Deville's experiment on dissociation.

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 small volume of 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, he says, 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 be enhanced 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: $A+BC \rightleftharpoons AB+C$. 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, the **active mass.**

Thus, *in reversible reactions, the extent of chemical change is proportional to the active masses of the interacting substances.* This is known as **the law of mass-action.** 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

The law may be illustrated by an experiment due to J. H. Gladstone (1855) Ferric chloride and ammonium thiocyanate react in solution to produce ferric thiocyanate, which has a blood-red colour The reaction is reversible : $FeCl_3 + 3NH_4CNS \rightleftharpoons Fe(CNS)_3 + 3NH_4Cl$, and if an excess of $FeCl_3$ or NH_4CNS is added the intensity of the colour deepens But if NH_4Cl is added, the reverse reaction is favoured by the action of mass and the colour becomes paler.

EXPT 2 —Prepare two solutions containing 2·7 gm of crystallised ferric chloride ($FeCl_3,6H_2O$), and 23 gm. of NH_4CNS, 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 (mols) per litre* If a gas mixture contains 3 65 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

The general equation of mass-action, due to Guldberg and Waage (1864–67), can now be stated. Let the reaction

$$A + B + C + \ldots \rightleftharpoons A' + B' + C' + \ldots$$

occur, and let it be reversible. In equilibrium :

$$\frac{[A'][B'][C'] \ldots}{[A]\,[B]\,[C] \ldots} = K,$$

where K is the **equilibrium constant.**

We shall usually 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: $3NH_4CNS + FeCl_3 \rightleftharpoons Fe(CNS)_3 + 3NH_4Cl$, 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.

Kinetic deduction of the law of mass-action.—We may consider the law of mass-action as an experimental fact. It may, however, be deduced (1) from thermodynamics; (2) from the kinetic theory A sketch of the second method, due to Guldberg and Waage, will be given here.

Consider the formation of gaseous hydrogen iodide from hydrogen and iodine. Molecules of HI can be formed only as the result of *collisions* of iodine and hydrogen molecules, the number of collisions per second being proportional to the number of molecules of each gas present in unit volume, *i.e.*, to its concentration. It is therefore proportional to the product of these concentrations, $k\,[H_2] \times [I_2]$ Every collision may not result in the formation of hydrogen iodide, but a definite fraction x of the total number of collisions will be effective; hence the rate of formation of HI 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 decomposition of HI will be $k_2[HI]^2$, since *two* HI molecules must collide, and the probability for this is proportional to $[HI]^2$.

The two reactions: (*a*) $H_2 + I_2 \rightarrow 2HI$, (*b*) $2HI \rightarrow H_2 + I_2$, go on simultaneously; hence:

$$\begin{aligned}\text{Rate of formation of HI} &= \text{Rate of combination of } H_2 \text{ and } I_2 \text{ to HI} - \text{Rate of decomposition of HI}\\ &= k_1\,[H_2] \times [I_2] - k_2\,[HI]^2.\end{aligned}$$

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:

$$\begin{aligned} k_1\,[H_2] \times [I_2] - k_2\,[HI]^2 &= 0;\\ \therefore\ k_1\,[H_2]\,[I_2] &= k_2\,[HI]^2,\\ \text{or}\quad \frac{[HI]^2}{[H_2]\,[I_2]} &= \frac{k_1}{k_2} = K.\end{aligned}$$

At a given temperature, K is constant: it is the equilibrium constant. It is independent of the amounts of iodine, hydrogen, and hydrogen iodide originally taken, but depends on the temperature.

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 energy. When a molecule acquires this **critical increment** of energy it becomes active

The number of bimolecular collisions in a mixture of hydrogen and iodine vapour can be calculated from the kinetic theory. At room temperature at atmospheric pressure this number is readily found to be of the order of 10^8, it is, further, proportional to $\sqrt{T}$. Experiments show, however, that the rate of chemical change is much smaller than would be expected if every collision were effective and also that it increases with rise of temperature much faster than $\sqrt{T}$. In fact, the velocity of most chemical reactions is approximately doubled for a rise of 10° C.

In order to explain such results, it is assumed that reaction on collision occurs only when the colliding molecules are **activated**, or possess energies above the average value for the temperature of the gas. The effect of temperature is then explained if it is assumed that the proportion of active molecules increases with temperature according to an exponential factor $e^{-q/kT}$, where k is Boltzmann's constant (p. 386) and q is the **energy of activation**; per mol $Q = \mathbf{N}_0 q$.

The number of collisions per second of *one* molecule with other molecules in a gas containing N molecules of mass m and diameter σ, per cm.^{3} is

$$N\sigma^2\left(\frac{4\pi kT}{m}\right)^{\frac{1}{2}}.$$

For $T = 273$, $\sigma = 10^{-8}$ cm, $k = 1{\cdot}37 \times 10^{-16}$, $N = 2{\cdot}7 \times 10^{19}$ and $m = 1{\cdot}65M \times 10^{-24}$ (M = molecular weight), this gives, as stated, a value of about 10^8. Actually, the *effective* collisions are about one per second in nearly all ordinary gas reactions at this 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 (at S.T P) were formed. Now at S.T P. 2×127 gm. of iodine (I_2) occupy 22,420 c c.

$\therefore$ vol of I_2 vapour at S.T.P. initially present

$$= \frac{22420 \times 0{\cdot}0601}{2 \times 127} = 5{\cdot}30 \text{ c c.}$$

The 9 52 c c of HI are formed from 4 76 c c. of H_2 and 4·76 c c. of I_2 $\therefore$ in equilibrium:

vol of $H_2 = 7{\cdot}94 - 4\ 76 = 3{\cdot}18$ c c ($4{\cdot}76 = 0{\cdot}5 \times$ vol of HI $= 0{\cdot}5 \times 9{\cdot}52$).

vol. of $I_2 = 5\ 30 - 4{\cdot}76 = 0{\cdot}54$ c.c.

vol of HI = 9·52. Hence, if V is the volume of the bulb in litres, the *concentrations* are: $[H_2] = 3{\cdot}18/22420V$; $[I_2] = 0{\cdot}54/22420V$; $[HI] = 9{\cdot}52/22420V$.

Hence. $$K = \frac{[H_2] \times [I_2]}{[HI]^2} = \frac{3{\cdot}18 \times 0{\cdot}54}{(9{\cdot}52)^2} = 0{\cdot}01895.$$

Now, suppose 8·10 c c of hydrogen and 2·94 c c of iodine vapour (at S T P.) heated at 444° What volume of HI will be formed in equilibrium ? Let $2x$ c c be formed

$$\begin{array}{lccccc} & H_2 & + & I_2 & \rightleftharpoons & 2HI \\ \text{Volumes .} & (8{\cdot}10-x) & & (2\ 94-x) & & 2x \end{array}$$

$$\therefore \frac{(8{\cdot}10-x)(2{\cdot}94-x)}{4x^2}=0\ 01895\ ;$$

$\therefore x=2{\cdot}825$ or $9{\cdot}12$ Only the root 2 83 is admissible, since 2 94 c c of I_2 vapour can give only 5 88 c c of HI as a maximum Thus, the volume of HI formed $=2\times 2\ 83$ c c. $=5{\cdot}63$ 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 It is easily shown that the extent of dissociation of hydrogen iodide is unaffected by pressure Let 2 gm. mols be heated in a volume V and let the degree of dissociation (p. 125) be γ. The numbers of gram molecules present in equilibrium are :

$$\begin{array}{ccccc} 2HI & \rightleftharpoons & H_2 & + & I_2, \\ 2(1-\gamma) & & \gamma & & \gamma \end{array}$$

hence the concentrations are :

$$[HI]=2(1-\gamma)/V\ ;\ [H_2]=\gamma/V\ ;\ [I_2]=\gamma/V\ ;$$
$$\therefore K=[H_2][I_2]/[HI]=\gamma^2/4(1-\gamma)^2,$$

which is independent of the volume V, and therefore of the pressure. This result is obtained in all cases where the total volume is unchanged by the reaction. If an increase of volume occurs, the extent of dissociation can be measured from the vapour density. This is the case with phosphorus pentachloride .

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

Let V be the volume and γ the extent of dissociation, then the concentrations are :

$$[PCl_5]=(1-\gamma)/V,$$
$$[PCl_3]=\gamma/V\ ;\ [Cl_2]=\gamma/V\ ;$$
$$\therefore \frac{[PCl_3][Cl_2]}{[PCl_5]}=\frac{\gamma^2}{(1-\gamma)V}=K.$$

The extent of dissociation now depends on the volume, V, and therefore on the pressure.

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 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 **Le Chatelier's 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 equilibrium. If the temperature of a 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 evolved at constant volume 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

$$\log K_2 - \log K_1 = \frac{Q_v}{4\ 576}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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 at 200° Find the pressure developed if PCl_5 is 48·5 per cent dissociated under 1 atm pressure at 200° C.

2·0 gm of $PCl_5 = 2\ 0/208 = 0\ 0096$ gm mol. Let x = degree of dissociation under the conditions of experiment Let the volumes be measured in litres ; then

$$[PCl_5] = \frac{0\ 0096(1-x)}{0\ 2},\quad [PCl_3] = [Cl_2] = \frac{0\ 0096x}{0{\cdot}2},\quad \therefore K = \frac{0{\cdot}0096x^2}{0{\cdot}2(1-x)} \quad \ldots(1)$$

At 200° under 1 atm pressure PCl_5 is 48·5 per cent. dissociated The volume of 1 gm mol. under these conditions is (see p 125)

$$22{\cdot}4 \times 1{\cdot}485 \times \frac{473}{273} = 57{\cdot}6 \text{ litres.}$$

Hence

$$K = \frac{(0{\cdot}485)^2}{0{\cdot}515 \times 57\ 6} = 0{\cdot}00793. \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

From the two expressions for K we find, on solving the quadratic equation, $x = 0\ 332$.

There are thus $1{\cdot}332 \times 0{\cdot}0096$ gm mols in 200 c c , and the pressure is therefore

$$1{\cdot}332 \times 0{\cdot}0096 \times \frac{22{\cdot}4}{0\,2} \times \frac{473}{273} = 2\,48 \text{ atm}$$

The degree of dissociation is reduced from 0 485 to 0 332 when the pressure is raised from 1 to 2·48 atm

Effect of addition of products of dissociation.—The effect of adding an excess of one of the products of dissociation *at constant volume* is obvious from the law of mass-action. In the case of the dissociation of hydrogen iodide

$$\frac{[H_2]\,[I_2]}{[HI]_2} = K,$$

addition of excess of H_2 or I_2 vapour will cause an increase of $[H_2]$ or $[I_2]$ respectively (since V is constant), hence to maintain the value of K, [HI] must also increase, *i.e* , the extent of dissociation is diminished. The same effect is produced by adding excess of Cl_2 or PCl_3 vapour to partly dissociated PCl_5, since in this case

$$\frac{[PCl_3][Cl_2]}{[PCl_5]} = K,$$

and increase of $[PCl_3]$ or $[Cl_2]$ must be followed by an increase of $[PCl_5]$ in order to maintain K constant.

The effect of adding an excess of one of the products of dissociation *at constant pressure*, however, requires more detailed examination.

Let 2 mols of HI be heated at 444°, then (see p. 314)

$$\frac{\gamma^2}{4(1-\gamma)^2} = K = 0{\cdot}01895\ ;$$

$$\therefore\ \gamma/(1-\gamma) = \pm\sqrt{0\ 0758} = \pm 0\ 2754\ ;\quad \therefore\ \gamma = 0\ 216$$

Now suppose a further 1 mol of H_2 be added, the pressure remaining constant, and let γ change to γ'. Then .

$$\begin{array}{ccccc} 2HI & \rightleftharpoons & H_2 & + & I_2, \\ 2(1-\gamma') & & \gamma'+1 & & \gamma', \end{array}$$

hence the total number of mols is

$$n = 2(1-\gamma') + \gamma' + 1 + \gamma' = 3.$$

The total volume is $V' = nRT/p = 3RT/p$;

$$\therefore\ [HI] = \frac{2(1-\gamma')p}{3RT},\ [H_2] = \frac{(\gamma'+1)p}{3RT},\ [I_2] = \frac{\gamma' p}{3RT};$$

$$\therefore\ K = \frac{\gamma'(1+\gamma')}{4(1-\gamma')^2} = 0{\cdot}01895\ ;$$

$\therefore\ \gamma' = 0{\cdot}063$ (the negative root being inadmissible). Hence *the dissociation is reduced.*

Now consider the case of PCl_5. Let 1 mol be heated at 200° at

1 atm pressure and let a further 2 mols of PCl_5 vapour be added at constant *pressure*. If γ' is the degree of dissociation (previously 0·485),

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$1-\gamma' \quad 2+\gamma' \quad \gamma';$$
$$\therefore\ V' = nRT/p = (3+\gamma')RT/p = (3+\gamma')RT\ (p = 1\text{ atm}),$$
$$\therefore\ [PCl_5] = \frac{1-\gamma'}{RT(3+\gamma')},\ [PCl_3] = \frac{2+\gamma'}{RT(3+\gamma')},\ [Cl_2] = \frac{\gamma'}{RT(3+\gamma')};$$
$$\therefore\ K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\gamma'(2+\gamma')}{RT(3+\gamma')(1-\gamma')} = 0\,00793$$

Now $R = 0{\cdot}08208$ litre atm. (p. 122) $T = 273+200 = 473$; $\therefore\ RT = 38\ 824$,

$$\therefore\ \frac{\gamma'(2+\gamma')}{(3+\gamma')(1-\gamma')} = 0{\cdot}3079;\quad \therefore\ x = 0{\cdot}306,$$

the other root being inadmissible Hence *the dissociation is 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.

Heterogeneous reactions.—The law of mass-action applies only to homogeneous systems (gases; solutions), since it is an essential part of the theory of Berthollet (p. 309) that when solids, for example, are present their active masses are constant and they can intervene in reversible reactions only by their vapours or in solution The vapour pressures and solubilities are constant when solid is present and in the expression for the law of mass-action *for the gaseous (or homogeneous solution) phase*, the concentrations of these substances are constant at a given temperature, and may be included in K, the equilibrium constant.

As an example, we may consider the action of steam on red-hot iron:

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

In the gaseous phase, to which alone the law of mass-action applies, we may consider that in addition to H_2O and H_2 at measurable and variable pressures, there are present also the vapours of the iron and oxide of iron at immeasurably small and constant pressures. In

$$K' = \frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4},$$

since $[Fe_3O_4]$ and $[Fe]$ are constant, we can write.

$$K' = \frac{[Fe_3O_4]}{[Fe]^3} \cdot \frac{[H_2]^4}{[H_2O]^4} = k \cdot \frac{[H_2]^4}{[H_2O]^4},$$

or
$$K = [H_2]/[H_2O],$$

where
$$K = \sqrt[4]{K'/k}.$$

This shows that the ratio of the concentrations (or partial pressures) or hydrogen and steam will be constant, at a given temperature, independent of the amounts of solid iron or iron oxide present

Electrolytic dissociation.—If a salt, acid, or base is dissolved in water its molecules are broken up into ions If the ionisation is incomplete, the **degree of ionisation**, α, will increase with dilution to a limiting value 1, when dissociation is complete Let 1 mol of electrolyte be dissolved in a volume V. Let us consider the case of the ionisation of a weak acid :

$$\underset{1-\alpha}{HA} \rightleftharpoons \underset{\alpha}{H^{\cdot}} + \underset{\alpha}{A'}.$$

The concentrations are then :

$$[HA]=(1-\alpha)/V;\ [H^{\cdot}]=[A']=\alpha/V.$$

If the law of mass-action applies to ionsation we shall have :

$$\frac{[H^{\cdot}][A']}{[HA]}=\frac{\alpha^2}{(1-\alpha)V}=K.$$

This equation is known as **Ostwald's dilution law** (1888) It applies to weak acids, as may be seen from the values of K, the **ionisation constant** for acetic acid on p. 253, and also to weak bases, such as ammonia $NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'$. In the case of strong electrolytes, however, such as potassium chloride, it fails completely. Such electrolytes are now supposed to be completely ionised in dilute solutions.

Solubility product.—If solid sodium chloride is in contact with its saturated solution we have two connected equilibria :

$$NaCl\ (solid) \rightleftharpoons NaCl\ (dissd.) \rightleftharpoons Na^{\cdot} + Cl'.$$

If the law of mass-action applied to the ions we should have: $[Na^{\cdot}]\times[Cl']=K[NaCl]$ But [NaCl], the concentration of unionised salt, is zero in the modern theory of strong electrolytes. In Arrhenius's theory it was assumed that [NaCl] is 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 is *equal* to the solubility product, the solution is in *equilibrium* with the solid, since then the concentration of unionised 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 occurs, unless the solution remains supersaturated.

The value of the ionic product, $[Na^{\cdot}] \times [Cl']$, 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 precipitated until the ionic product becomes equal to the solubility product. The other ion of the added electrolyte, $H^{\cdot}$, has no effect, 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 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'.

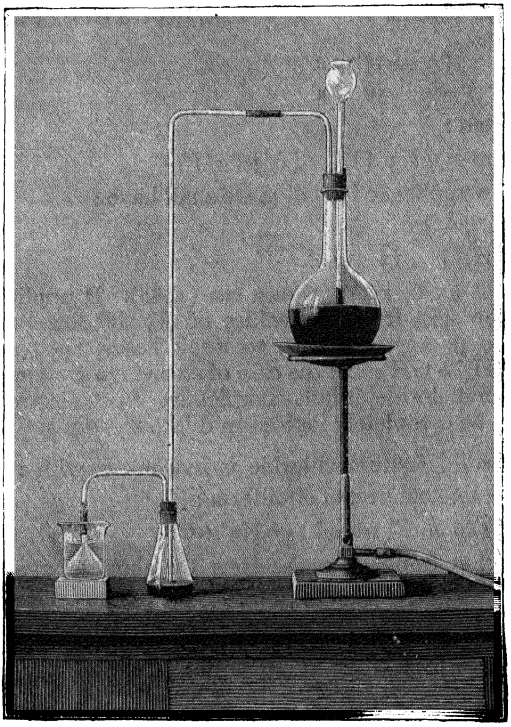


FIG. 160.—Preparation of pure sodium chloride.

Although Arrhenius's theory of the solubility product is not in agreement with the modern theory of strong electrolytes (p. 321), and does not agree with experiment in the case of salts so readily soluble as sodium chloride, it is in *qualitative* agreement with experiment in nearly all cases and hence it has been given here.

EXPT. 3.—Pass gaseous hydrogen chloride into a filtered saturated solution of common salt, which contains magnesium chloride as impurity, using the apparatus shown in Fig. 160. A white crystalline powder of NaCl falls. This is filtered off in a Büchner funnel, dried on

a porous plate, and heated carefully in a dish to drive off hydrochloric acid, it is then pure

EXPT 4.—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.

The effect of adding *excess of a reagent* in analytical chemistry is clear from the solubility product theory. 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 either silver nitrate or a chloride is added to the clear filtrate, an opalescence is produced, owing to precipitation of AgCl. A trace of the latter existed in solution, 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: $H_2AgCl_3 \rightleftharpoons 2H + AgCl_3''$. As a general rule, too great an excess of reagent should not be added in precipitation reactions.

EXPT 5.—To a dilute 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 redissolves, and the solution 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, **potassium argentocyanide,** the silver is present in the anion, and the solution is practically free from silver ions, $Ag^{\cdot}$. It gives 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.

Strong electrolytes.—It has long been known that the Ostwald dilution formula does not apply to solutions of strong acid or bases, or solutions of largely ionised salts, *i.e.*, to *strong* electrolytes (p. 259). Since the law of mass-action fails for strong electrolytes the law of solubility product will not apply to them strictly, although it does so in a qualitative form, as experiments show.

In the modern theory (p. 260), the strong electrolytes are practically completely ionised in dilute solutions, and since no un-ionised substance

is present the law of mass-action cannot apply. Instead of the solubility product equation

$$c_C \times c_A = \text{const} = K$$

for the constancy of the product of the *concentrations* of the cation C and anion A, of a salt, we must now write .

$$a_C \times a_A = \text{const.} = K',$$

where a denotes the *activity* (p. 281) We may replace a by fc, where f is the *activity coefficient*, which depends on the concentration and is not a constant as would be required by the law of mass-action , hence

$$a_C \quad a_A = (c_C \cdot f_C) \times (c_A \cdot f_A) = K'$$

The law of mass-action applies if activities are substituted for concentrations In very dilute solutions the activity coefficients (which are proportional to $1 - k\sqrt{c}$) become nearly unity, and when the solubility of the salt and hence the concentrations of its ions are small, the solubility product law is very approximately true This is seen from the following results for the solubilities of silver nitrite in presence of silver nitrate or potassium nitrite The concentrations are in mols per litre

Conc of $AgNO_3$ or KNO_2	Solubility of $AgNO_2$ in presence of		Solubility calcd.
	$AgNO_3$	KNO_2	
0	0 0269	0 0269	0 0269
0·00258	0 0260	0 0259	0 0259
0·00588	0 0244	0·0249	0 0247
0 02355	0 0192	0 0203	0·0187

Hydrolysis.—Salts formed from weak acids, or weak bases, or both, are decomposed in aqueous solution with production of free acid and base This reaction is called hydrolysis. The salts themselves are usually largely ionised in solution (p. 260) ; the weak acid or base is only slightly ionised and its ionisation is also further repressed by the ion of the salt which is common to the acid or base. The hydrolysis is most simply represented as due to the withdrawal of $H^·$ or OH' ions from the water (p. 248) by the anion or cation of the salt, so forming the weak acid or base, the other ion of the water remaining free and exhibiting an alkaline or acid reaction. Although only traces of $H^·$ and OH' ions are present in water, further ionisation occurs when one ion is withdrawn, since the product of the concentrations is constant . $[H^·] \times [OH'] = K_w$. Thus, when the $H^·$ ion is withdrawn to form a weak acid, an appreciable concentration of OH' ions results, and the solution shows an alkaline reaction, *e.g.*, with potassium cyanide

$$K^· + CN' + (H^· + OH') \rightleftharpoons K^· + OH' + HCN.$$

The ionisation of the very weak hydrocyanic acid, $HCN \rightleftharpoons H^{\cdot} + CN'$, is almost entirely suppressed by the action of the large excess of cyanide ion in the solution The solution smells of hydrocyanic acid.

A salt of a strong acid and weak base hydrolyses to the weak base by withdrawal of OH' ions, and shows an acid reaction in solution; in a solution of ferric chloride, ferric hydroxide is produced and exists in a state of colloidal solution showing a dark red colour, and the solution has an acid reaction ·

$$Fe''' + 3Cl' + 3(H^{\cdot} + OH') \rightleftharpoons Fe(OH)_3 + 3H^{\cdot} + 3Cl'.$$

A solution of a salt of a weak acid and weak base is hydrolysed, *e.g.*, ammonium carbonate

$$(NH_4)_2CO_3 + 2H_2O \rightleftharpoons \begin{array}{ccc} 2NH_4OH & + & H_2CO_3 \\ \Downarrow & & \Downarrow \\ 2(NH^{\cdot}_4 + OH') & & H^{\cdot} + HCO_3' \end{array}$$

Since in this case the base is stronger than the acid (p. 259 ; cf p. 550), the solution reacts alkaline.

An application of the law of mass-action to hydrolysis .

$$[\text{acid}] \times [\text{base}]/[\text{salt}] \times [\text{water}] = \text{const} = K_h$$

shows that the extent of hydrolysis increases with dilution, except in the case of a salt of a very weak base and very weak acid, when it is practically independent of dilution. The extent of hydrolysis increases with rise in temperature

EXPT 6.—Add phenolphthalein to a concentrated solution of borax and acetic acid till the pink colour *just* disappears Dilute the solution: the pink colour reappears

$$Na_2B_4O_7 + 3H_2O \rightleftharpoons 2NaBO_2 + 2H_3BO_3,$$
$$NaBO_2 + 2H_2O \rightleftharpoons NaOH + H_3BO_3$$

The boric acid also produced is so weak an acid that it has no action on the indicator, the caustic soda, a strong base, turns it pink.

EXPT 7.—Pour 2 to 3 c c of 30 per cent. ferric chloride solution into 500 c c. of boiling distilled water A deep red solution of colloidal ferric hydroxide is formed $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$.

EXPT. 8.—Add phenolphthalein to a *concentrated* solution of sodium sulphite and heat The pink liquid becomes colourless on cooling, but the colour reappears on heating (Raschig).

Buffer solutions.—A solution can be prepared which contains a definite concentration of hydrogen ions which is not altered by dilution. This is called a buffer solution. An example is a solution

Buffer solutions.—A solution can be prepared which contains a definite concentration of hydrogen ions which is not altered by dilution. This is called a buffer solution. An example is a solution containing sodium acetate and acetic acid (a weak acid) For the acid we have

$$[H^+] \times [Ac']/[HAc] = \text{const.} = K_a.$$

Now add Ac′ ions in the form of sodium acetate, NaAc This salt is practically completely ionised and the ionisation of the weak acetic acid is almost entirely repressed by the addition of the acetate, since the equilibrium $HAc \rightleftharpoons H^+ + Ac'$ is shifted to the left almost completely by the mass-action of the Ac′ of the sodium acetate. Hence we can put .

$[HAc]$ = original total acid concentration = [acid],

$[Ac']$ = NaAc total concentration = [Salt] ,

$$\therefore [H^+] = K_a[HAc]/[Ac']$$

$$= K_a \frac{[\text{acid}]}{[\text{salt}]},$$

which is independent of dilution, since [acid]/[salt] remains practically unchanged. In a solution containing equivalent amounts of acid and salt, $[H^+] = K_a$.

Theory of indicators.—The action of acids and alkalies in changing the colour of indicators has since the time of Boyle been 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, and **turmeric**, from the ground root of the *Curcuma longa* of India (used in making curries) which is yellow, turned reddish-brown by alkalies or boric acid.

Many synthetic organic substances are now used as indicators. **Methyl-orange** is turned yellow by alkalies and red by acids , **para-nitrophenol** 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 bright red by traces of alkali , **alizarin red** is turned deep purple by alkalies, yellow by acids

According to **Ostwald's theory of indicators** (1891) 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, *para*-nitrophenol is a weak acid, colourless in the undissociated state. A trace of strong acid drives back the slight dissociation of the weakly acidic indicator, and the pale yellow solution becomes colourless. If an alkali is added, the OH' ions combine with the H^+ ions of the indicator to form H_2O molecules, and further ionisation of the indicator

the neutral molecule to form an ion, this does not necessarily affect the above theory of indicators.

Phenolphthalein functions 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*-nitrophenol.

Methyl-orange is the sodium salt of a sulphonic acid,

$$(CH_3)_2N \cdot R \cdot SO_3Na,$$

where R is $-C_6H_4 \cdot N=N \cdot C_6H_4-$, and is largely ionised in solution. The anion $(CH_3)_2N \cdot R \cdot \bar{S}O_3$ is yellow. In presence of acids this behaves as a weak base and attaches a proton to form an ion $\overset{+}{H}N(CH_3)_2N \cdot R \cdot \bar{S}O_3$ having opposite charges on different parts but neutral as a whole (a hybrid ion). The change of colour is thus due to the reaction:

$$\overset{+}{H}N(CH_3)_2 \cdot R \cdot \bar{S}O_3 \text{ (red)} + \bar{O}H \rightleftharpoons (CH_3)_2N \cdot R \cdot \bar{S}O_3 \text{ (yellow)} + H_2O.$$

Sensitiveness of indicators.—An indicator requires a definite concentration of H· 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· ions.

The ionic product $[H\cdot] \times [OH'] = 10^{-13\cdot8}$ at 18°. The OH′ concentration required to produce a colour change of an indicator may, therefore, always be represented by the equivalent H concentration $[OH'] = [OH'] \times [H]/[H] = 10^{-13\cdot8}/[H]$. At the **neutral point** the H· and OH′ concentrations are equal, each being equal to its concentration in pure water $[H] = [OH'] = \sqrt{10^{-13\cdot8}} = 10^{-6\cdot9}$. If [H] is greater than $10^{-6\cdot9}$ the solution is *acid*, if it is less than $10^{-6\cdot9}$, *e.g.*, 10^{-8}, the solution is *alkaline*. The concentration of H ions may be represented by minus the exponent of the concentration, and is then usually written *p*H, *e.g.*, if $[H] = 10^{-8\cdot1}$, *p*H = 8·1. An **ideal indicator**, which shows the exact point of neutrality, corresponds with *p*H = 6·9.

The values of [H] and *p*H required to produce colour changes of various indicators are given in the table below, compiled from the results of Salm (1907) and Sorensen (1909).

The gaps are to be filled in with the colour next adjoining, *e.g.*, phenolphthalein is colourless with all H 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· $[H\cdot] = [OH'] = 10^{-6\cdot9}$, with phenolphthalein the solution would be still faintly alkaline, with methyl-orange it is slightly acid

(0·0005N), whilst methyl-violet requires 0·01N-acid to produce a colour change

Colour of Indicator with Hydrogen Ion concentration normal multiplied by	$[H]=N$	pH	Indicator					
			Methyl-violet	Methyl-orange	Congo red	Methyl-red	Litmus	Phenol-phthalein
	2		Golden-yellow					
	1	0	Green					
	10^{-1}	1	Greenish-blue					
	10^{-2}	2	Blue	Red				
	10^{-3}	3	Violet	Orange-red	Blue	Violet-red		
	10^{-4}	4		Orange-yellow	Violet	Red		
	10^{-5}	5			Scarlet	Orange-yellow		
	10^{-6}	6				Yellow	Red	
	10^{-7}	7					Blue	Colourless
	10^{-8}	8						Rose-red
	10^{-9}	9						Red
	10^{-10}	10						
Indicator solution per cent			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. 9.—Three rows of flasks, each containing 100 c.c. of "conductivity" water, are supported on a rack (Fig. 161) with milk-glass shelves. To the flasks of each row are added solutions of phenolphthalein, litmus, p-nitrophenol (pH 5–7), methyl-red and methyl-orange, 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 NH_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 **methyl formate** freshly distilled over dry potassium carbonate is poured simultaneously into all the flasks of this row. The methyl formate slowly hydrolyses, giving formic acid and methyl alcohol (neutral):

$$H{\cdot}COOCH_3 + H_2O = H{\cdot}COOH + CH_3OH.$$

The H' ions of the formic acid neutralise the OH' ions of the baryta, and then excess of H' 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).

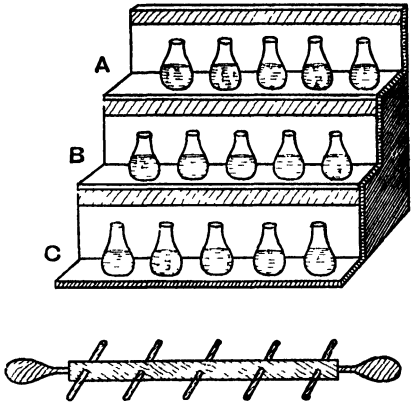


FIG 161 —Experiment on indicators

Choice of indicators. — In acidimetry and alkalimetry, the choice of indicator depends on the hydrogen-ion concentration of the resulting salt If a slightly alkaline salt like sodium acetate is formed at the equivalent point, an indicator is used which will show a change in colour on the alkaline side Phenolphthalein, which changes colour for pH about 8 to 10, is therefore used in titrating acetic acid with sodium hydroxide If a weak base like ammonia is being titrated with a strong acid, the resulting acid-reacting salt will require an indicator which changes colour on the acid side of neutrality In this case, methyl-red, which changes at pH about 4 to 6, may be used When a highly ionised neutral salt is formed, as in titrating a strong acid with a strong base, a slight excess of either solution makes a large change in pH, so that any indicator having a colour change between pH 3 and 10 will be satisfactory Conversely, the titration of a very weak base with a very weak acid is seldom possible, on account of the relatively small change in pH value at the end-point.

An important application of indicators is the determination of hydrogen ion concentration An indicator is added to the unknown solution, and the tint compared with a series of reference solutions, containing the same indicator but varying H concentrations These standard solutions are " buffered " to definite pH values by mixtures such as borax and boric acid, or sodium acetate and acetic acid (p 324) The actual pH may be confirmed by hydrogen electrode measurements (p 866). The effect of salts, proteins, etc., on the indicator must be considered, and corrections applied.

SUMMARY OF CHAPTER XX

The cause of chemical change is identified with the **affinities** of the interacting substances. 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 gram 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, is constant when equilibrium is attained* :

$$A + B + C + \ldots \rightleftharpoons D + E + F \ldots$$

$$\frac{[D] \times [E] \times [F] \ldots}{[A] \times [B] \times [C] \ldots} = K, \text{ where } K \text{ is the equilibrium constant.}$$

If a system in equilibrium is subjected to an increase of pressure, a reaction will occur if possible leading to a diminution of volume, *i e* to a decrease in pressure If a system in equilibrium is subjected to a rise in temperature a reaction will take place which is accompanied by an absorption of heat, *i e.* one which tends to lower the temperature.

These results are special cases of **Le Chatelier's law of reaction,** which states that *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 adding an excess of one of the products of dissociation, either at constant volume or at constant pressure, on the degree of dissociation of a gas may be calculated by the law of mass-action

In heterogeneous reactions the law of mass-action applies to the gaseous or dissolved components The concentrations of the liquids or solids in the gas phase or solution are constant, and may be included in the equilibrium constant, K

The law of mass-action applies to the ionisation of weak electrolytes (**Ostwald's dilution law**), but not to strong electrolytes, when the concentrations must be replaced by the activities.

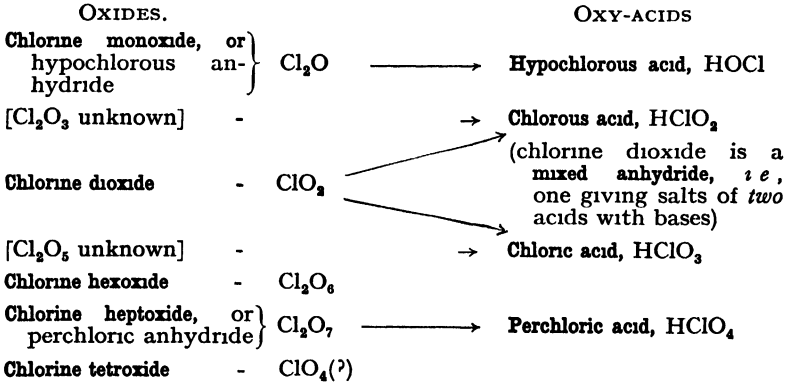
The effect of addition of a common ion on the solubility of a salt (**solubility product**), and the results of **hydrolysis,** may be considered from the point of view of the law of mass-action

Indicators are weakly acid or basic substances, with anions or cations of different colour from the unionised molecules.

CHAPTER XXI

THE OXIDES AND OXY-ACIDS OF CHLORINE

The known **oxides and oxy-acids of chlorine** are summarised in the following table:



The action of chlorine on alkalies: hypochlorites.—When a stream of chlorine is passed through a cold solution of caustic potash so that excess of alkali remains, a liquid smelling like chlorine, but with a difference, is obtained. This liquid, discovered by Berthollet in 1789, is more stable than chlorine water and was used under the name of *eau de Javelle* for bleaching. In England about 1798 the absorption was carried out with milk of lime. Tennant, of St Rollox (Glasgow), in 1799 found that chlorine is absorbed by dry slaked-lime, and the product, called **bleaching powder**, gave a bleaching liquor on treatment with water.

Balard, in 1834, showed that these bleaching substances contain salts of **hypochlorous acid**, HOCl. The reactions lead to the formation of a mixture of a **hypochlorite** and chloride:

$$2KOH + Cl_2 = KCl + KOCl + H_2O;$$
$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O.$$

With caustic soda a solution containing **sodium hypochlorite**, NaOCl, and sodium chloride, is formed. This is also produced by adding sodium carbonate 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, 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.

Acids, even carbonic acid, *e g*, atmospheric carbon dioxide, liberate the very weak hypochlorous acid from its salts; solutions of these smell of the free acid when exposed to air, and exhibit bleaching properties.

EXPT 1.—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 it 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 The remaining hypochlorous acid is removed by washing, and finally by treating with a substance such as sodium thiosulphate, which decomposes the hypochlorous acid and is hence called an **antichlor** Paper pulp, prepared from wood, is bleached with sodium hypochlorite solution and acid

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: $Cl_2 + H_2O \rightleftharpoons HCl + HOCl \rightleftharpoons H + Cl' + HOCl$, is reversible.

The equations: $Cl_2 + H_2O = 2HCl + O$, and $HOCl = HCl + O$, 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 is converted into inert chloride. It is the available *oxygen* liberated from HOCl which causes the bleaching action.

The constitution of chlorine water may be proved by experiment. 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 goes on practically to completion. But if chlorine water is boiled in a flask under a reflux condenser, 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. In $N/20$ chlorine water about 30 per cent, and in $N/100$ about 70 per cent., of the chlorine is hydrolysed into HOCl and HCl.

Chlorates.—If chlorine is passed through a solution of caustic potash or soda, the hypochlorite produced so long as the liquid remains alkaline is rapidly converted with evolution of heat into chlorate when excess of chlorine is present $3KOCl = KClO_3 + 2KCl$

EXPT 2.—The apparatus is shown in Fig 160. Chlorine generated from manganese dioxide and hydrochloric acid is 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 of **potassium chlorate**, $KClO_3$, which separate The crystals are washed once or twice with a little cold water and then recrystallised from hot water. They are sparingly soluble in cold water (8 395 gm per 100 gm water at 25°), are monoclinic in shape (Fig 162), easily distinguishable from the cubes of chloride, and on heating in a test-tube melt and evolve oxygen, leaving potassium chloride

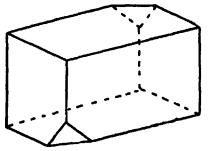


FIG 162.—Crystal of potassium chlorate

The total 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 it was called *hyperoxymuriate of potash.* Potassium chlorate gives certain reactions characteristic of all chlorates

(1) Solutions 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 $3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + 2ClO_2$ On warming there is a crackling noise, due to explosions of the ClO_2.

(4) Potassium chlorate warmed with concentrated hydrochloric acid gives off a yellow gas (*euchlorine*), consisting of a mixture of Cl_2 and ClO_2. $8KClO_3 + 24HCl = 8KCl + 12H_2O + 9Cl_2 + 6ClO_2$.

Potassium chlorate detonates violently when triturated with phosphorus or sulphur (*Dangerous*). A mixture of the chlorate and sulphur detonates on percussion.

Perchlorates.—In the decomposition of potassium chlorate by heat, **potassium perchlorate,** $KClO_4$, is formed: $4KClO_3 = 3KClO_4 + KCl$. This may also be prepared by fusing potassium chlorate with barium peroxide, extracting with hot water, and crystallising:

$$KClO_3 + BaO_2 = KClO_4 + BaO.$$

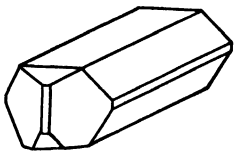


FIG. 163 —Crystal of potassium perchlorate

The salt was discovered by Stadion in 1815 The orthorhombic crystalline form of the perchlorate (Fig. 163) differs from the form of the chlorate

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.

Chlorine monoxide.—This gas is obtained by distilling concentrated hypochlorous acid under reduced pressure · $2HOCl \rightleftharpoons Cl_2O + H_2O$, but is usually prepared by the action of dry chlorine on yellow precipitated oxide of mercury, previously heated to 300°–400°, contained in a cooled tube (Fig 164). A brown oxychloride of mercury remains, and brownish-yellow chlorine monoxide gas passes on :

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

It is condensed in a freezing mixture to an orange-coloured liquid, b. pt. 2·0°. The gas may be collected by downward displacement; it attacks mercury, but only slowly, 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 being absorbed by caustic soda solution. Liquid chlorine monoxide 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 decom-

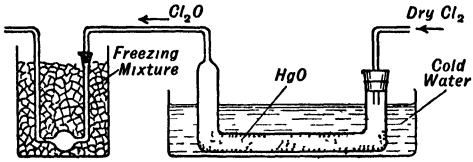


FIG 164.—Preparation of chlorine monoxide.

posed by the gas, with production of chlorine $Cl_2O + 2HCl = 2Cl_2 + H_2O$. The gas dissolves easily in water, forming a golden-yellow solution containing **hypochlorous acid**: $Cl_2O + H_2O \rightleftharpoons 2HOCl$.

Hypochlorous acid.—This acid is known only in solution On distillation the solution 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 and a dilute solution of hypochlorous acid collects in the receiver.

An interesting reaction is the formation of hypochlorous acid by the direct oxidation of hydrochloric acid, discovered by Odling in 1860: $HCl + O = HOCl$. A current of air is passed through concentrated hydrochloric acid in a wash-bottle, and then through potassium permanganate solution in a retort heated on a water bath, hypochlorous acid distils over.

Hypochlorous acid is most conveniently prepared from bleaching powder. When dissolved in water, this decomposes into chloride and hypochlorite: $2Ca(OCl)Cl = CaCl_2 + Ca(OCl)_2$. 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.

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 capable of liberating hydrochloric acid from calcium chloride is added to bleaching powder, or its solution, the whole of the chlorine is expelled as such

$$Ca(OCl)_2 + CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 2Cl_2$$

Free hypochlorous acid is produced by the action of chlorine on a solution of a hypochlorite:

$$KOCl + Cl_2 + H_2O = KCl + 2HOCl.$$

This reaction probably occurs in two stages, as follows :

(*a*) $H_2O + Cl_2 \rightleftharpoons HCl + HOCl \rightleftharpoons H^{\cdot} + Cl' + HOCl.$

(*b*) $OCl' + H = HOCl.$

If chlorine is passed through a suspension of sodium bicarbonate or precipitated calcium carbonate in water, or a solution of sodium sulphate or phosphate, hypochlorous acid (not a hypochlorite) is formed :

$$2Cl_2 + H_2O + CaCO_3 = 2HOCl + CaCl_2 + CO_2$$

This reaction probably proceeds in two stages

(i) $Cl_2 + H_2O \rightleftharpoons HCl + HOCl \rightleftharpoons H^{\cdot} + Cl' + HOCl$,

(ii) $2H + CO_3'' \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2 + H_2O$, $H^{\cdot} + SO_4'' \rightleftharpoons HSO_4'$, etc.

The hypochlorous acid produced is too weak to decompose the carbonate with formation of a hypochlorite The function of the carbonate, etc , is to remove the hydrochloric acid as fast as it is produced, and so to prevent reaction (i) coming to a standstill

Hypochlorous acid in solution is pale golden yellow, or colourless when dilute It is 0·02 per cent ionised in $N/10$ solution. 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) $HOCl + 2O$ (nascent) $= HClO_3$.

The decomposition is accelerated by platinum black, manganese dioxide, or cobalt oxide. Hypochlorites on heating with the latter oxide in alkaline solution rapidly evolve oxygen : $2NaOCl = 2NaCl + O_2$. With concentrated acids they evolve chlorine.

Hypochlorous acid precipitates silver nitrate solution :

$$3HOCl + 3AgNO_3 = 3HNO_3 + 2AgCl + AgClO_3.$$

Chloric and perchloric acids give no precipitate with silver nitrate.

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 and its salts evolve oxygen :

$$OCl' + H_2O_2 = Cl' + H_2O + O_2.$$

Hypochlorous acid is a powerful oxidising and bleaching agent, due to the liberation of nascent oxygen : $HOCl = HCl + O$.

EXPT. 3.—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 becomes brown, and is converted into hydrated manganic oxide $Mn(OH)_2 + NaOCl + H_2O = Mn(OH)_4 + NaCl$

EXPT 4.—To a solution of chrome alum add excess of NaOCl solution 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 *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.

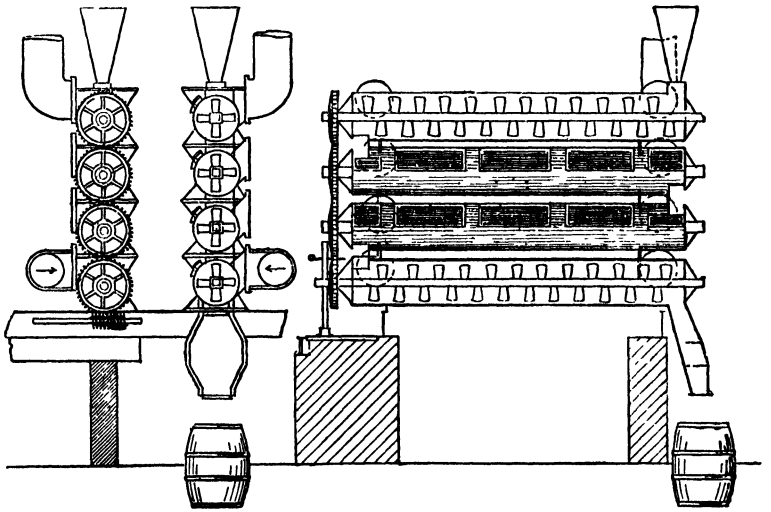


FIG 165.—Hasenclever bleaching powder apparatus

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, 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 35–39 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 165) 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: $Ca(OCl)_2 + CaCl_2$ Stahlschmidt assumed that it contained the compound $Ca(OH)(OCl)$: according to Lunge, free lime is not an essential constituent, but is due to the particles of lime becoming encrusted with bleaching powder and so escaping complete chlorination. He 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 alcohol. Moist carbon dioxide at 70° sets free *the whole* of the available chlorine from bleaching powder, whilst it has no action on calcium chloride: $CaOCl_2 + CO_2 = CaCO_3 + Cl_2$.

These results agree with the formula proposed by Odling, according to which the active constituent of bleaching powder is a compound of the formula $Ca\begin{<}{OCl}{Cl}$, *i.e.*, **calcium chloro-hypochlorite,** formed from a molecule each of hydrochloric and hypochlorous acids:

$$Ca\begin{<}{OH}{OH} + \begin{matrix}HOCl\\HCl\end{matrix} = Ca\begin{<}{OCl}{Cl} + \begin{matrix}H_2O\\H_2O\end{matrix}$$

Stahlschmidt's formula, $Ca(OH)OCl$, 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 formulae of Balard, Stahlschmidt and Odling 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 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
4	Found - -		1 2	1 1	1 2

Thus, only Odling's formula agrees with the experimental results

Recent experimenters (Ditz, Neumann) consider that the free lime in ordinary bleaching powder is an essential constituent, and that combined water is also present. Normal bleaching powder is regarded as the compound $3Ca(OCl)Cl, Ca(OH)_2, 5H_2O$. In complete absence of moisture a very hygroscopic compound $3Ca(OCl)Cl, Ca(OH)_2, 3H_2O$ is formed, whilst at low temperatures $Ca(OCl)Cl, Ca(OH)_2, H_2O$ can be obtained. The active constituent is Odling's compound.

Available chlorine of bleaching powder.—Bleaching powder is mainly employed as an oxidising agent, and the active agent is really nascent oxygen. Usually the chlorine equivalent of this active oxygen is returned as the available chlorine $O(16) = Cl_2(71)$ If 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 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.

Commercial bleaching powder always contains some free lime, as well as 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** : A suspension of bleaching powder is 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 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 $N/10$ $As_2O_3 = 0{\cdot}00355$ gm of active Cl

2 **Bunsen and Wagner's method**: A suspension of bleaching powder is treated with excess of potassium iodide solution, and acidified with acetic acid Iodine is liberated $2KI + HOCl + 2CH_3COOH = 2CH_3 \cdot COOK$ (potassium acetate) $+ I_2 + H_2O + HCl$ 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) $+ 2NaI$ A little starch-paste is then added, and the titration continued until the blue colour, due to the iodine, vanishes 1 c c of $N/10$ $Na_2S_2O_3 = 0{\cdot}00355$ 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 sometimes used 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 $Cl = 22{\cdot}4 \times 71/16 = 99{\cdot}5$ per cent). The crystalline hydrate, $Ca(OCl)_2,4H_2O$, is first deposited on evaporation.

Chlorine dioxide.—Thos. Hoyle in 1798 obtained a yellow explosive gas from potassium chlorate and concentrated sulphuric acid, but did not recognise it as an oxide of chlorine. The gas was also obtained by Chenevix, but its composition was first ascertained by Davy in 1815 He showed that it was chlorine dioxide, ClO_2. On explosion, two volumes of this gas gave three volumes of gas, consisting of two volumes of oxygen and one volume of chlorine: $2ClO_2 = Cl_2 + 2O_2$. The density of chlorine dioxide gas was found by Pebal and Schacherl (1882) to correspond with the formula ClO_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 slowly, being completely absorbed by it There is considerable danger of violent explosion in the preparation of chlorine dioxide and it is recommended that no attempt should be made to prepare it by this method

The reaction $3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + 2ClO_2$ appears to take place as follows

$$KClO_3 + H_2SO_4 = KHSO_4 + HClO_3 \text{ (chloric acid)};$$
$$3HClO_3 = HClO_4 \text{ (perchloric acid)} + 2ClO_2 + H_2O.$$

Pure chlorine dioxide is prepared by passing dry chlorine over silver chlorate at 90° and condensing it from the gas in a freezing mixture (King and Partington, 1926)

$$2AgClO_3 + Cl_2 = 2AgCl + 2ClO_2 + O_2.$$

When passed through a tube cooled in a freezing mixture the gas condenses to a dark red liquid, boiling at 11·0°, and at −59° this freezes to an orange-coloured crystalline solid The liquid and solid are slowly decomposed by exposure to light 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, according to some experimenters at 60°–63°, by an electric spark, and in contact with turpentine, alcohol, or ether.

Expt. 5.—Add one c c of cold concentrated sulphuric acid to two portions of 0 5 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 Care must be used in these experiments, as some acid is usually projected from the tubes

Chlorine dioxide (sometimes called **chlorine peroxide**) is a powerful oxidising agent This is evident from the following experiments, due to Hoyle and to Fourcroy and Vauquelin.

Expt 6 —Equal parts of powdered sugar (or starch) and potassium chlorate are mixed with a spatula on a sand bath, 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 7 —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 *carefully* poured down a thistle

funnel on to the chlorate, ClO_2 is evolved When this comes in contact with the phosphorus, there is a series of flashes of light, accompanied by slight and harmless explosions

Chlorine hexoxide, Cl_2O_6, discovered by Millon in 1843, but overlooked until 1925, when it was obtained again by Bodenstein, is formed as a red liquid, m pt $-1°$, density 1 65, when chlorine dioxide or a mixture of chlorine and ozone is exposed to light

Chlorine tetroxide, $(ClO_4)_x$ (where x probably $=2$) is said to be obtained in stable o $1N$ ethereal solution by the action of iodine on silver perchlorate (Gomberg, 1923).

$$2AgClO_4 + I_2 = 2AgI + (ClO_4)_2$$

Chlorous acid.—Chlorine dioxide dissolves in water, forming a yellow solution without acid reaction which is stable for several weeks in the dark at 0°. With solutions of alkalies, however, it acts as an acidic oxide, forming a mixture of two salts in equivalent amounts: $2KOH + 2ClO_2 = KClO_3 + KClO_2 + H_2O$. $KClO_2$ is the salt of chlorous acid, $HClO_2$ The salts may be separated by evaporation *in vacuo* over sulphuric acid, when the less soluble $KClO_3$ is first deposited.

Pure chlorites are obtained by the action of alkali and hydrogen peroxide on a concentrated aqueous solution of chlorine dioxide. The latter is conveniently prepared by warming at 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 $2ClO_2 + H_2O_2 = 2HClO_2 + O_2$. Barium chlorite is formed by suspending barium peroxide in hydrogen peroxide and passing in chlorine dioxide Free chlorous acid is obtained in solution by treating barium chlorite with dilute sulphuric acid

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 has been used for detonators.

Chlorites liberate iodine from iodides:

$$NaClO_2 + 4KI + 2H_2O = 2I_2 + 4KOH + NaCl$$

They react only slowly with arsenious oxide Chlorous acid gives a characteristic violet colour with ferrous sulphate

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 (1843), was shown by Garzarolli-Thurnlack in 1881 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, Cl_2O, called **euchlorine** (p. 332), was examined by Pebal in 1875, and the method used was applied by Garzarolli-Thurnlack to the supposed trioxide

A measured volume of the gas was decomposed 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.—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 more convenient to start with barium chlorate, a solution of which is precipitated with sulphuric acid · $Ba(ClO_3)_2 + H_2SO_4 = BaSO_4$ (ppd) $+ 2HClO_3$ The excess of sulphuric acid is precipitated with baryta water, the solution is decanted and is 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 . $2NaClO_3 + BaCl_2 \rightleftharpoons 2NaCl + Ba(ClO_3)_2$. The sodium chloride is deposited, and the hot filtered solution is evaporated, when monoclinic crystals of $Ba(ClO_3)_2,H_2O$ separate. Chloric acid was first 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 and becomes yellow. Organic substances, such as cotton-wool or paper, are ignited by the concentrated acid. It has a pungent smell, rather like that of nitric

acid, and strong acidic and bleaching properties. The anhydride corresponding with chloric acid, $2HClO_3 - H_2O = Cl_2O_5$, is not known.

EXPT 8.—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.

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 is not reduced.

Perchloric acid.—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 crude sodium nitrate, or Chile nitre. It acts 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:

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O.$$

Potassium perchlorate, $KClO_4$, is prepared by heating the *pure* chlorate at 510° in a new porcelain dish, or better at 480° in a silica flask for 8 hours, separating from the chloride by treatment with cold water and crystallising the residue from hot water. $4KClO_3 = 3KClO_4 + KCl$. 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. −17·8°); $2HClO_4,5H_2O$ (m. pt. −30°); $2HClO_4,7H_2O$ (m. pt. −41·4°) and two forms of $HClO_4,3H_2O$ (m. pt.

$-43{\cdot}2°$ and $-37°$). The anhydrous acid explodes violently at 92° and sometimes spontaneously on keeping, when it undergoes decomposition. It 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 71 6 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.

$$NH_4ClO_4 + HCl = NH_4Cl + HClO_4,$$
$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O,$$
$$2NH_4Cl + 3Cl_2 = N_2 + 8HCl.$$

Paper and wood catch fire when anhydrous perchloric acid 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 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 Silver perchlorate is peculiar in being a metallic salt which is soluble in toluene

Chlorine Heptoxide.—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. 166), until the reaction is complete :

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$$

The reaction appears to take place with the intermediate formation of free 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 .

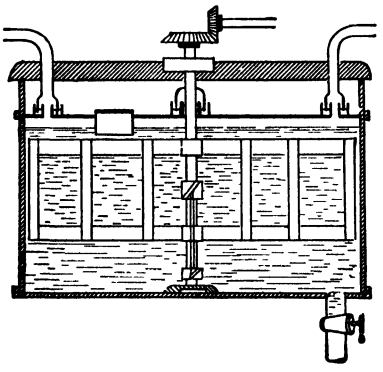


FIG 166 —Manufacture of calcium chlorate

$$Ca(OCl)_2 = CaCl_2 + O_2$$

Alkaline hypochlorite solutions may be boiled without much decomposition, but oxygen is slowly evolved, traces of chlorites being also formed

$$2KOCl = KCl + KClO_2$$

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

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 The chloride is first completely converted into *chlorate*; on prolonged electrolysis, this passes into *perchlorate* Chlorates are used as oxidising agents (*e g.*, in the oxidation of aniline to aniline black), as weed killers, and in making fireworks Perchlorates are employed in the manufacture of detonators and explosives.

The action of the free hypochlorous acid as a carrier of oxygen to the hypochlorite in the formation of chlorate may, according to Foerster (1899), be represented as follows As long as the liquid remains alkaline, chloride and hypochlorite are produced

$$1.\ Cl_2 + 2OH' = Cl' + OCl' + H_2O.$$

When all the alkali is removed, the hypochlorite ion reacts with the free hypochlorous acid, producing chlorate and chloride ions .

$$2.\ OCl' + 2HOCl = ClO_3' + 2Cl' + 2H^{\cdot}.$$

The hypochlorite and hydrogen ions then form hypochlorous acid, and the latter reacts again according to (2)

$$3\ H^{\cdot} + OCl' = HOCl$$

If we multiply equation (1) by 3, (3) by 2, and add, we obtain the usual equation for the total reaction

$$3Cl_2 + 6OH' = ClO_3' + 5Cl' + 3H_2O$$

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 or mineral oil, in other words from chemical processes The value of a fuel is not determined by its chemical constituents, since these are almost entirely dissipated and lost in ashes and gases during combustion, but by the amount of *energy* in the form of heat or work which can be obtained by combustion

The heat, Q_v, evolved in a chemical reaction occurring at constant volume (so that no work is done) is a measure of the diminution of energy, *i e*, the energy of the initial system, U_1, minus the energy of the final system, U_2:

$$Q_v = U_1 - U_2 = -\Delta U.$$

How much energy is associated with each system we have no certain means of judging ; all that can be determined is the difference between the energies of the system before and after change has occurred. This difference is evolved as heat, and may be measured.

In reactions involving gases, 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, A, must be applied to the heat, Q_p, 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 therefore distinguish between **heat of reaction at constant volume**, Q_v, and **heat of reaction at constant pressure**, Q_p

A mixture of 2 016 gm of H_2 and 16 gm of O_2 at 0° and 1 atm pressure occupies 22,412 + 11,206 = 33,618 c c If this is converted to liquid water at 0°, the latter will occupy 18 c c There has been a diminution in volume of 33,618 − 18 = 33,600 c c , and since the atmospheric pressure is equal to 76 × 13 595 × 980 6 dynes per sq cm , the work done by the atmospheric pressure on the system, which appears as heat, is 33,600 × 76 × 13 595 × 980 6 = 3 404 × 10^{10} ergs = 3·404 × 10^{10}/4 184 × 10^7 g. cal = 813 6 g cal The observed heat of reaction at constant pressure, Q_p, is 68,450 g cal , hence the heat of reaction at constant volume, Q_v, is 68,450 − 814 = 67,636 g cal This latter value represents the difference between the chemical energies of the hydrogen and oxygen gases, and that of the liquid water Thus

$$H_2 + \tfrac{1}{2}O_2 = H_2O \text{ (liq)} + 68{,}450 \text{ g cal (constant pressure) ;}$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O \text{ (liq)} + 67{,}636 \text{ g cal (constant volume)}$$

If the reaction occurred at 100°, with production of steam, the heat evolved at constant pressure is diminished by the latent heat of steam, 18 × 538 g 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 of constant heat summation** (1840) It enables one to calculate many heats of reaction which could not be determined directly

EXAMPLE 1 —Find the heat of formation per mol of carbon monoxide, CO, from solid carbon and gaseous oxygen, given the following data

Heat of combustion of carbon to carbon dioxide $C + O_2 = CO_2$ + 94 k cal

Heat of combustion of carbon monoxide to dioxide $CO + \tfrac{1}{2}O_2 = CO_2 + 67{\cdot}8$ k. cal.

By subtracting the second of these equations from the first, we find :
Heat of formation of carbon monoxide $C + \tfrac{1}{2}O_2 = CO + 26{\cdot}2$ k cal.

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** are tabulated per *mol* of compound produced.

The values are in k. cal for room temperature. Round brackets ( ) denote that the substances are gases, square brackets [ ] that they are solids, liquids are written without brackets. Sulphur is the rhombic (α) form, carbon is taken as graphite.

HEATS OF FORMATION.

$(H_2)+\frac{1}{2}(O_2)=H_2O$	68 5	$2[P]+\frac{5}{2}(O_2)=[P_2O_5]$	370
$(H_2)+\frac{1}{2}(O_2)=(H_2O)$	57 8	$[C]+(O_2)=(CO_2)$	94
$(H_2)+(O_2)=H_2O_2$	46 8	$[C]+\frac{1}{2}(O_2)=(CO)$	26 2
$\frac{1}{2}(H_2)+\frac{1}{2}(Cl_2)=(HCl)$	22 0	$[C]+2[S]=CS_2$	−19 6
$\frac{1}{2}(H_2)+\frac{1}{2}Br_2=(HBr)$	8 4	$[Na]+\frac{1}{2}(Cl_2)=[NaCl]$	97 7
$\frac{1}{2}(H_2)+\frac{1}{2}[I_2]=(HI)$	−6 1	$[Na]+\frac{1}{2}Br_2=[NaBr]$	85 8
$(H_2)+[S]=(H_2S)$	5	$[Na]+\frac{1}{2}[I_2]=[NaI]$	69 1
$\frac{1}{2}(N_2)+\frac{3}{2}(H_2)=(NH_3)$	12	$[Ag]+\frac{1}{2}(Cl_2)=[AgCl]$	30 6
$[P]+\frac{3}{2}(H_2)=(PH_3)$	−5 8	$[Ag]+\frac{1}{2}Br_2=[AgBr]$	24
$[As]+\frac{3}{2}(H_2)=(AsH_3)$	−44	$[Ag]+\frac{1}{2}[I_2]=[AgI]$	15
$\frac{1}{2}(N_2)+\frac{1}{2}(O_2)=(NO)$	−21 6	$[Ca]+(Cl_2)=[CaCl_2]$	191
$(N_2)+\frac{1}{2}(O_2)=(N_2O)$	−17 7	$[Sr]+(Cl_2)=[SrCl_2]$	198
$[S]+(O_2)=(SO_2)$	96	$[Ba]+(Cl_2)=[BaCl_2]$	205
$[S]+\frac{3}{2}(O_2)=[SO_3]$	91 9	$[Fe]+\frac{3}{2}(Cl_2)=[FeCl_3]$	96

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 = sum of heats of formation of final compounds − sum of heats 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 $[Cu]+(Cl_2)=[CuCl_2]+51\ 6$ k. cal may be written in the form $0+0=[CuCl_2]+51{\cdot}6$ k cal, or $[CuCl_2]=-51\ 6$ k cal, indicating that $[CuCl_2]$ contains 51·6 k 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 1.—Find the heat of the reaction.

$$[CaCl_2]+2[Na]=[Ca]+2[NaCl]+x.$$

The heats of formation of $CaCl_2$ and NaCl are 191 k cal. and 97·7 k. cal, respectively, hence ·

$$-191 = -2 \times 97{\cdot}7 + x, \quad \text{or} \quad x = 4{\cdot}4 \text{ k cal}$$

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 : $(NH_3) + Aq = NH_3,Aq + 8400$ g. cal means that when 17 grams of ammonia gas dissolve in a large quantity of water, 8400 g. 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 :

$$HClO_4 + Aq = HClO_4,Aq + 20{,}100 \text{ g. cal.}$$

EXAMPLE 2 —Find the heat of formation of gaseous hydrogen iodide from hydrogen and solid iodine from the following heats of reaction .

1. $(HI) + Aq = HI\ Aq. + 19\ 20$ k cal
2. $KOH\ Aq. + HI\ Aq = KI\ Aq + 13\ 57$ k cal
3. $KI\ Aq + \frac{1}{2}(Cl_2) = [I] + KCl\ Aq + 26\ 21$ k cal
4. $KOH\ Aq + HCl\ Aq = KCl\ Aq + 13{\cdot}74$ k. cal
5. $\frac{1}{2}(H_2) + \frac{1}{2}(Cl_2) = (HCl) + 22\ 0$ k cal.
6. $(HCl) + Aq. = HCl\ Aq + 17{\cdot}32$ k cal

We write (4), (5) and (6) in the reverse order underneath (1), (2) and (3) and add all the equations, when we find

$$\frac{1}{2}(H_2) + [1] = (HI) - 5\ 93 \text{ k cal}$$

Heats of formation from the atoms.—Heats of reaction always refer to the substances taking part in the reaction in the actual states in which they are used. The heat of combustion of carbon in the form of diamond in gaseous oxygen to form carbon dioxide is somewhat different from the heat of combustion of graphite, since these two forms of solid carbon contain different amounts of energy, whereas the same final product is obtained in each case The heat of combustion of methane, CH_4, is not equal to the sum of the heats of combustion of solid carbon and two molecules of gaseous hydrogen, since in the formation of methane from these substances the carbon has been converted into a gas and the hydrogen molecules have been resolved into atoms of hydrogen. If we knew the heat of evaporation of solid carbon, the heat of dissociation of molecular hydrogen into atoms of hydrogen, and the heat of formation of methane from solid carbon and hydrogen gas, we could calculate the heat of formation of gaseous methane from gaseous carbon atoms and gaseous hydrogen atoms. In a similar way, it would be possible to calculate heats of formation of gaseous compounds from the gaseous elements in the

atomic state if data for heats of evaporation of the ordinary solid substances, and of dissociation of molecules into atoms, were known.

It is possible to calculate, mainly from spectroscopic data, several such heats of dissociation into normal *atoms*, which are given in the following table in k. cal (*absorbed*)

H_2	100·5	$CO = C + O$	240	HF	185
Cl_2	57	$NO = N + O$	157	HCl	101
Br_2	45·2	S_2	113	HBr	86
I_2	35 2	Se_2	83	HI	68
O_2	118	Te_2	65	H_2O	240
N_2	210			H_2S	175
				NH_3	294
				CH_4	362

The heat of volatilisation of carbon (12 gm) is calculated as 140 k cal

EXAMPLE 3 —Calculate the heat of formation of methane, CH_4, from the gaseous atomic elements

$$[C] + 2(H_2) = (CH_4) + 18\ 6 \text{ k cal.}$$
$$(C) = [C] + 140 \text{ k cal}$$
$$4(H) = 2(H_2) + 201 \text{ k cal ;}$$
$$\therefore \text{ by addition . } (C) + 4(H) = (CH_4) + 359\ 6 \text{ k cal.}$$

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 of chlorine, ozone and hydrogen peroxide, on the other hand, are all unstable substances, decomposing spontaneously, or when heated, or when brought in contact with other substances. There are also different *degrees of stability*, *e g.*, the stability of perchloric acid is greater than that of hypochlorous acid.

It is of interest to inquire into the *causes of stability* (or otherwise) of substances. Formerly only certain empirical rules, which had numerous exceptions, were available.

Thus, the stability of a compound depends on the **electrochemical character** of its component elements. Compounds of strongly electropositive with strongly electronegative elements are usually stable, *e g.*, $\overset{+}{K}\overset{-}{Cl}$, whilst compounds of elements of the same electrochemical character are usually unstable, *e g* , $\overset{-}{Cl}_2\overset{-}{O}$, $\overset{+}{Pd}_2\overset{+}{H}$ An exception is the stable $\overset{-}{P}_2\overset{-}{O}_5$. Again, the stability of a compound alters with the **valency** of an element contained in it : $\overset{IV}{PtCl_4}$ decomposes at 374° into $\overset{II}{PtCl_2}$ and

Cl_2; $PtCl_2$ is decomposed only at 582°, 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 triple bonds · ethane, $CH_3 CH_3$, is quite stable, whereas acetylene, CH·CH, is explosive

The principal condition affecting the stability of a substance, however, is the **energy content.**

Water, hydrogen chloride, potassium chloride, and methane are formed from their elements with considerable evolution of heat, or loss of energy—*i e*, they are strongly **exothermic compounds.** They contain considerably less energy than the elements from which they are produced, and they are *stable*

The compounds chlorine monoxide, hypochlorous acid, chloric acid, and perchloric acid are formed 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 stability is roughly in proportion to the amount of energy evolved in formation; thus, perchloric acid in solution 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.

$$(Cl_2) + \tfrac{1}{2}(O_2) = (Cl_2O) - 25{\cdot}1 \text{ k cal.}$$
$$\tfrac{1}{2}(Cl_2) + \tfrac{1}{2}(O_2) + \tfrac{1}{2}(H_2) + \text{Aq.} = HOCl,\text{Aq} + 29{\cdot}9 \text{ k cal.}$$
$$\tfrac{1}{2}(Cl_2) + \tfrac{1}{2}(O_2) + \tfrac{1}{2}(H_2) + \text{Aq.} = HClO_3,\text{Aq} + 23{\cdot}9 \text{ k cal.}$$
$$\tfrac{1}{2}(Cl_2) + 2(O_2) + \tfrac{1}{2}(H_2) + \text{Aq} = HClO_4,\text{Aq.} + 39{\cdot}1 \text{ k. cal.}$$

Free energy.—Although the heat evolution, or diminution of **total energy,** gives an approximate measure of the stability of a compound, it is really the content of **free energy** which determines its stability Of the total energy diminution, part is in general convertible into work by suitable means, whilst the other part appears as heat The part convertible into work is the free energy. For example, the reaction

$$Zn + CuSO_4 \text{ Aq} = ZnSO_4 \text{ Aq.} + Cu,$$

as it occurs in the ordinary way evolves heat, but when it occurs in the Daniell cell part of the energy change is obtainable as electrical energy, which in turn is (theoretically) completely convertible into work It is this free energy change which provides an accurate measure of the tendency of the system $Zn + CuSO_4$, Aq. to pass spontaneously into the system $Cu + ZnSO_4$, Aq, *i e.*, which provides a measure of the relative stability of the two systems *Only those changes can occur spontaneously which are attended by a diminution of free energy.* The corresponding statement for the total energy, to the effect that only those reactions

occur spontaneously which are attended by evolution of heat, was stated by Thomsen and Berthelot, although the latter had the correct idea in mind when he called it the **principle of maximum work.** This principle is very often, as we have seen, approximately true and is a useful guide. The statement is true at the absolute zero, and in many reactions between solids and liquids it holds approximately The correct statement of the principle forms what is known as **Nernst's Heat Theorem** (1906) this enables us in many cases to calculate equilibrium constants from heats of reaction.

The constitution of the oxy-compounds of chlorine.—If we assumed chlorine to be univalent in all its oxygen compounds, except ClO_2, these would have the following formulae :

chlorine monoxide, Cl—O—Cl hypochlorous acid, H—O—Cl.

chlorine dioxide, $Cl<^{O}_{O}$ 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

Usually, however, the stability of compounds containing chains of singly-linked oxygen atoms decreases as the number of oxygen atoms in the chain increases. 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, $HClO_3$, $HClO_4$, whereas actually it increases.

Although the energy-content of the molecule is the main factor affecting stability, it is assumed that this is conditioned by the mode of linkage of the atoms, *i e* , by valency. The formulae of the above compounds are usually written with the chlorine atom with different valencies, from 1 to 7 (Blomstrand, 1869).

I. Cl—O—Cl , H—O—Cl

III and V. H—O—Cl=O ; H—O—$\overset{\text{III}}{\text{Cl}}<^{\text{O}}_{\text{O}}$, or H—O—$\overset{\text{V}}{\text{Cl}}(=\text{O})_2$.

II and IV. $\text{Cl}<^{\text{O}}_{\text{O}}$, or $\overset{\text{IV}}{\text{Cl}}(=\text{O})_2$.

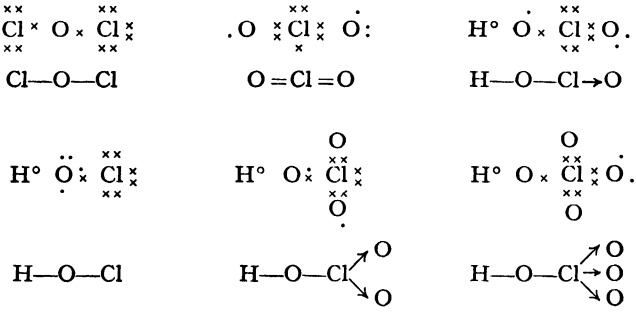
VII. $\text{O}_3\overset{\text{VII}}{\text{Cl}}—\text{O}—\overset{\text{VII}}{\text{Cl}}\text{O}_3$, H—O—$\text{Cl}<^{\text{O}}_{\text{O}}$O, or H—O—$\overset{\text{VII}}{\text{Cl}}(=\text{O})_3$

The hydrate $HClO_4,H_2O$ may be written . $(\text{HO})_2\overset{\text{VII}}{\text{Cl}}(=\text{O})_2\text{OH}$

The variable valency of iodine, an element very similar to chlorine

and univalent in its stable compounds, appears in the compounds ICl_3, IF_5, and IF_7

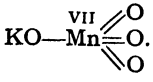
Electronic formulae.—The formulae for the oxides and oxy-acids of chlorine based on the modern electronic theory of valency, which is explained in Chapter XXXV, are somewhat different from the above. In some cases it is assumed that a pair of electrons necessary for the formation of a valency link and usually *shared* by two atoms, are provided by the same atom, when the formulae are as follows, the donation of a pair of electrons being shown by →



The oxygen electrons are denoted by dots, those of chlorine by crosses, that of hydrogen by a circle, an ordinary valency bond is formed by two atoms *sharing* a pair of electrons, a double bond by *four* shared electrons

Chlorine dioxide contains an odd electron (unpaired), and is a representative of the somewhat rare class of **odd molecules**, which are generally coloured, magnetic, and unstable. In the new formulae for $HClO_2$, $HClO_3$ and $HClO_4$ the oxygens other than that in the hydroxyl group (the hydrogen of which is ionisable) are attached by **coordination bonds**, or **semi-polar double bonds**, rather than by ordinary double bonds. The corresponding bromine and iodine compounds are similarly formulated Iodine, in addition, forms a very stable H_5IO_6, which can be formulated as $(HO)_5I \rightarrow O$

The element manganese, which occurs in the same group of the Periodic System as chlorine, is often assumed (cf p 954) to be heptavalent in the compound potassium permanganate, $KMnO_4$, which resembles the perchlorate in crystalline form .



CHAPTER XXII

THE HALOGENS

Bromine.

Bromine.—Bromine was discovered in 1826 by A J. Balard in the residues from the manufacture of sea salt at Montpellier, where he was assistant in the École de Pharmacie. These liquors, known as *bittern*, contain **magnesium bromide**, $MgBr_2$. On addition of chlorine, the liquid becomes yellow and gives an orange-red colour with starch-paste Bromine is liberated : $MgBr_2 + Cl_2 = MgCl_2 + Br_2$, or $2Br' + Cl_2 = 2Cl' + Br_2$. 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 it 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 chief sources of bromine are the magnesium, calcium and alkali bromides of certain mineral springs in America and Germany, and the residues of the Stassfurt potash deposits. 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, traces of which also occur in the Northwich brine Bromine in combination is found in sea animals and plants ; the ancient Tyrian purple, obtained from a shellfish, consists of a dibromo-indigo.

Preparation of bromine.—A bromine compound is **potassium bromide**, KBr, used in photography, and in medicine as a sedative. From this bromine can be obtained by heating with sulphuric acid and manganese dioxide :

$$2KBr + MnO_2 + 3H_2SO_4 = Br_2 + 2KHSO_4 + MnSO_4 + 2H_2O.$$

Expt. 1 —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 bromine vapour is condensed in a little water in the

receiver. A red solution of bromine, **bromine water**, is formed, and a small quantity of nearly black liquid bromine settles out at the bottom. 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

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 ·

$$2CuSO_4 + Na_2SO_3 + 2KI + H_2O = Na_2SO_4 + H_2SO_4 + 2CuI + K_2SO_4$$

Scott's method of preparation of pure hydrobromic acid (p. 358) is the simplest way of obtaining a pure bromine compound Traces of sulphuric and hydrobromic acids which may be present in almost pure bromine are removed by allowing it to stand over quicklime and anhydrous calcium bromide, and distilling

The technical preparation of bromine.—Attempts have been made to obtain bromine from sea-water. This is chlorinated and aniline added. Tribromoaniline, $C_6H_2Br_3NH_2$, is precipitated One lb of bromine is obtained from 1800 gallons of ordinary sea-water. Bromine is to be obtained from the Dead Sea.

Most of the bromine is prepared from brines or residual liquors containing bromides at Stassfurt or Michigan. These are decomposed by chlorine.

The liquor heated to about 60° trickles down a tower containing perforated shelves, or filled with earthenware balls. Steam is blown in at the bottom and chlorine gas is introduced about half-way 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 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) $+ 4CO_2$. A slight excess of chlorine is used, so as to displace all the bromine, and the amount of steam is sufficient to raise the liquid to the boiling point just before it leaves the bottom of the tower, and at the same time such that it is nearly all condensed by the cooler liquid in the upper part of the tower.

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 58·80°. The vapour density at 228° is 79·6, corresponding with the formula Br_2. At 1050° dissociation into atoms to the extent of 6·3 per cent. 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, and of lead tetraethyl for anti-knock motor fuel.

Bromine combines directly with many elements, forming bromides.

EXPT 2.—Five c c of bromine are poured into a test-glass standing inside a bell-jar over a draught-hole in the bench The top of the jar is closed by a glass plate 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 dull 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

Bromine vapour bleaches moist litmus paper, though more slowly than chlorine. Starch-paste is coloured orange-yellow by bromine water or vapour. In water, 3·6 parts of bromine dissolve in 100 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 6·2° into bromine water and bromine.

Chloroform, benzene, and carbon disulphide abstract bromine from its aqueous solution, forming orange-red liquids.

EXPT 3.—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 sodium 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 converted AgCl into AgBr. The results agree with Stas's values The value has been found from the density of hydrogen bromide 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 (H = 1) or 79·92 (O = 16).

Hydrobromic acid.—Bromine vapour unites directly with hydrogen when the mixture is passed over heated charcoal or 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 from gaseous Br_2 is only 11 k. cal., as compared with 22 k. cal. with HCl.

EXPT 4.—Pure dry hydrogen is passed slowly through dry bromine contained in a bubbler, which may be warmed to 35°-40° in a water bath, when a mixture of hydrogen and bromine vapour is formed. This is passed through a hard glass tube containing platinised asbestos packed between plugs of glass wool. When the air has been expelled, the tube containing the platinised asbestos is heated to about 200°, when reaction commences and usually proceeds without further external heating. In order to remove any unconverted bromine vapour (which is present only when a fairly rapid stream of gas is used), the gas is passed through a tube packed with solid ferrous bromide, which absorbs the bromine vapour, and it is then passed through one or more tubes containing fused calcium bromide in order to dry the gas. If pure hydrogen bromide is required, the gas is condensed by cooling in liquid air, when the excess of hydrogen passes on and solid hydrogen bromide is obtained. This process, which is a modification of that used by Baxter (1931), is much superior to the use of an electrically heated platinum spiral generally described. Phosphorus pentoxide reacts slowly with hydrogen chloride and more slowly with hydrogen bromide, some $POCl_3$ and $POBr_3$ being formed. It decomposes hydrogen iodide.

Hydrogen bromide is 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.

The thermal dissociation of hydrogen bromide is given below, in percentages:

t° C. - - - -	727	1108	1220
% decomp. of HBr -	0·18	0·84	1·15

It is greater than that of hydrogen chloride but less than that of hydrogen iodide.

Hydrogen bromide is usually 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:

$$PBr_3 + 3H_2O = H_3PO_3 \text{ (phosphorous acid)} + 3HBr;$$
$$PBr_5 + 4H_2O = H_3PO_4 \text{ (phosphoric acid)} + 5HBr.$$

EXPT. 5.—Twenty gm of red phosphorus and 40 c.c. of water are placed in a flask, and 40 c c. of bromine are added *drop by drop* from a tap funnel (Fig. 168). The gas is passed through a U-tube loosely filled with broken glass smeared with moist red phosphorus. This removes unchanged bromine vapour The addition of the first few drops of bromine is attended by lambent green flames, but when the air is displaced these are not formed. At the end of the reaction the flask is gently heated The gas is collected by downward displacement in dry jars The jar is partly covered with a glass plate. The gas may be dried over calcium bromide and collected over mercury.

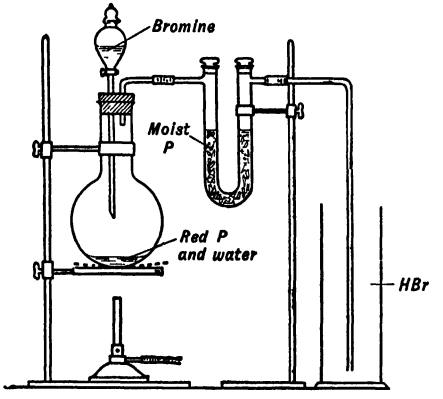


FIG 168.—Preparation of hydrogen bromide

Hydrogen bromide may be obtained by the action of bromine on benzene in presence of aluminium: $C_6H_6 + 2Br_2 = C_6H_4Br_2$ (dibromo-benzene) $+ 2HBr$. This is a reaction of substitution, two atoms of hydrogen are removed from the benzene molecule, and their place is taken by two atoms of bromine.

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) 40·5.
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 0°. The solution is a strong acid: $HBr \rightleftharpoons H' + Br'$. 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. 194). 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°. The solution saturated at 0° contains 69, that at 25°, 66 per cent. of HBr.

Aqueous hydrobromic acid may be prepared by passing the gas into water through an inverted retort, as shown in Fig. 169. 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.

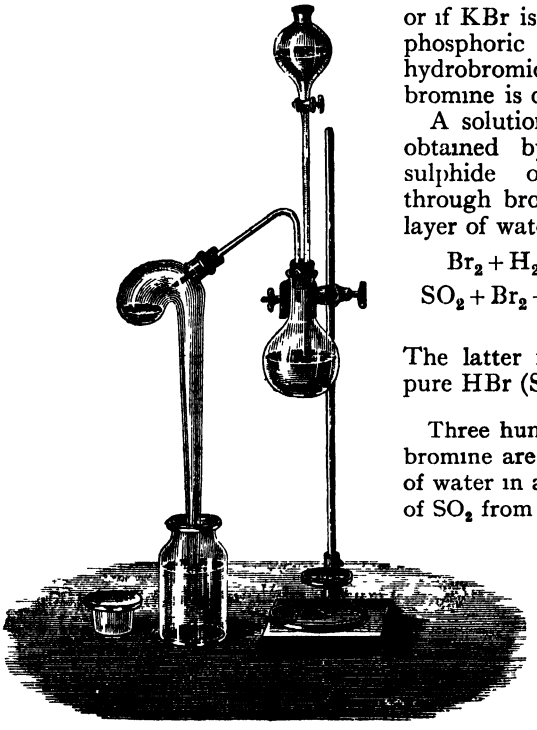


FIG 169.—Preparation of aqueous hydrobromic acid

A solution of the acid is also obtained by passing hydrogen sulphide 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 almost 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.

The solid hydrates, $HBr,2H_2O$, m. pt. $-11·2°$, $HBr,3H_2O$, m. pt. $-47·5°$, and $HBr,4H_2O$, m. pt. $-55·8°$, are formed on cooling very concentrated solutions.

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:

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

Bromides.—Hydrobromic acid 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 alkali bromides are obtained from bromide of iron (p. 354) or by dissolving bromine in a solution of alkali .

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O,$$

evaporating, and heating strongly to decompose the bromate :

$$2KBrO_3 = 2KBr + 3O_2.$$

The residue on evaporation may be mixed with powdered charcoal and heated, when the bromate is reduced at a lower temperature :

$$KBrO_3 + 3C = KBr + 3CO$$

The mass is warmed with water, filtered from excess of charcoal, and crystallised by evaporation.

Ammonium bromide free from bromate is obtained by the action of bromine on cooled ammonia solution ·

$$3Br_2 + 8NH_3 = 6NH_4Br + N_2.$$

Nearly all bromides are soluble in water , silver, lead, and mercurous bromides only very sparingly. Silver nitrate solution is used as a test 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 bromine vapour when the substance is heated with MnO_2 and H_2SO_4, are also characteristic reactions.

Oxygen compounds of bromine.—An **oxide** of bromine, Br_3O_8, is formed as a white, crystalline solid by the action of pure (100 per cent) ozone on purified bromine vapour at $-5°$ to $+10°$ under low pressure (Schumacher and Lewis, 1929). It appears to exist in two modifications, with a transition point at $-35°$ Indications of the existence of a gaseous oxide, of unknown composition, were obtained, but it is not stable in presence of bromine The oxide Br_3O_8 is stable at $-80°$, but unless the materials for its preparation are very pure and the apparatus very clean, an explosion results.

The following **oxy-acids** of bromine have been described :

Hypobromous acid, HBrO
Bromous acid, $HBrO_2$.
Bromic acid, $HBrO_3$.

Hypobromous acid.—By shaking bromine water with preciptated 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 straw-yellow liquid, decomposing when heated with production of bromine and bromic acid, and is a powerful oxidising and bleaching agent.

If bromine is dissolved in cold aqueous potash or soda, an unstable **hypobromite** is formed: $Br_2 + 2NaOH = NaBr + NaBrO + H_2O$. These are used as oxidising agents and in the estimation of hydrogen peroxide and of urea. On keeping, the solutions decompose with formation of bromide and bromate: $3NaOBr = 2NaBr + NaBrO_3$. Bromine vapour is 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, $HBrO_2$, 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.—When bromine is dissolved in hot concentrated alkali a solution of a **bromate** and a bromide is obtained:

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

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. Potassium bromate also separates out when bromine vapour is passed into a solution of potassium carbonate which has been saturated with chlorine: $6KOCl + Br_2 = 2KBrO_3 + 4KCl + Cl_2$.

Potassium bromate is formed by passing chlorine through alkaline bromide: $KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O$

When silver nitrate is added to a solution of potassium bromate, **silver bromate,** $AgBrO_3$, is precipitated. This is treated with bromine water; insoluble silver bromide is formed and the filtered solution contains **bromic acid**: $5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3$.

By evaporation on a water-bath, a 5 per cent. solution may be obtained. By concentration in a vacuum desiccator a 50 per cent. solution may be obtained, but more concentrated solutions give off bromine and oxygen: $4HBrO_3 = 2H_2O + 2Br_2 + 5O_2$. Bromic acid is a colourless liquid and 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 and are not at present known :

1. $KBrO_3$, $HgBrO_3$, and $AgBrO_3$, give bromide + oxygen ;

2. $Mg(BrO_3)_2$, $Zn(BrO_3)_2$, $Al(BrO_3)_3$, give oxide + bromine + oxygen : $Pb(BrO_3)_2$ and $Cu(BrO_3)_2$ give oxide and bromide.

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 .

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

Chlorine merely dissolves in liquid bromine and no compound has been obtained in the pure state, although BrCl appears from spectroscopic evidence to exist to some extent in a mixture of chlorine and bromine vapour.

IODINE.

Iodine.—In 1812 Courtois, of Paris, discovered that the mother-liquors from which soda had been crystallised in the manufacture from *varec*, or seaweed-ashes, gave off a violet vapour when heated with manganese dioxide and sulphuric acid. This vapour condensed to a black metallic-looking crystalline substance. The investigation of this material, called " the substance X," was begun by Clement and Desormes and continued 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 as a new element analogous to chlorine, and received the name iodine (from the Greek *ioides*, violet-coloured) on account of the beautiful violet colour of its vapour. It forms 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.) 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 or iodates, 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 preparation 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 technical preparation of iodine from seaweed was begun by Dr. Ure at Glasgow and is also carried out 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 **thyroxin**, $C_{15}H_{11}O_4NI_4$, 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 contained iodine, and the water which percolated 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 iodine passes into the lungs per twenty-four hours

The most important source of iodine is the alkali iodate (perhaps also some periodate) contained to the extent of 0·2 per cent. as $NaIO_3$ 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 6.—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 obtaining iodine from seaweed 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 and sodium sulphates, are fished out. On cooling, impure sodium chloride (" kelp salt ") separates, and on further evaporation crude potassium chloride 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* or *aludels* (Fig. 176) Manganese dioxide is added, and iodine distils off on heating, collecting in the udells. It

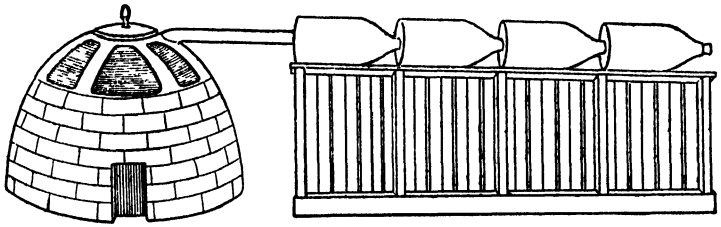


FIG 170 —The technical preparation of iodine

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.

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 lime-stone, and distilled with sulphuric acid and manganese dioxide This process seems to have been revived in Norway, the algin is sold as *Norgine* for use as an adhesive

The main source of iodine at the present day is the mother-liquor (" aqua vieja ") of *caliche* This is run into a wooden vat and treated with sodium hydrogen sulphite. The iodine precipitated is pressed, and resublimed.

The reaction has been variously represented, but it involves the reduction of the iodate to iodine and the oxidation of the sulphite to sulphate, *e g* , by the reaction :

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

Iodic acid is reduced by sulphurous acid :

$$2HIO_3 + 5H_2SO_3 = I_2 + 5H_2SO_4 + H_2O.$$

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 :

$$I_2 + H_2O + H_2SO_3 = 2HI + H_2SO_4 ;$$
$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

The above reactions involve the mutual decomposition of iodic acid and hydriodic acid : the former is an oxidising agent and the latter a reducing agent. Iodine appears only when all the free sulphurous acid is used up, and the whole process therefore exhibits a **period of induction.** This is shown in the following experiment, due to Landolt.

EXPT. 7.—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 of which are volatile, and cannot be separated by sublimation. Resublimation over potassium iodide removes most of the impurity.

EXPT 8.—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 strong 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 .

$$Cu_2I_2 + O_2 = 2CuO + I_2.$$

Baxter heated pure iodine pentoxide, from recrystallised iodic acid, at 300° in a platinum boat in a quartz tube $2I_2O_5 = 2I_2 + 5O_2$.

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. 171) 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:

		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 according to Victor Meyer 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. More recent experiments by Starck and Bodenstein (1910) give 45 per cent. dissociation at 1200°, and the extrapolation of their results would indicate that dissociation would be complete only at about 3000°. 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 spectrum consisting of a large number of equally-spaced lines.

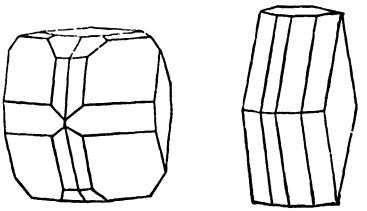


FIG 171 —Iodine crystals

Iodine is much less soluble in water than either chlorine or bromine, 1 part dissolves in 3616 parts of water at 18°, 2145 parts at 35°, and 1084 parts at 55°. The solution has a brownish-yellow colour. 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, H_2O, separate. Chloroform and carbon disulphide, which readily extract iodine from aqueous solutions, do not do so from solutions in potassium iodide. Many other polyiodides are known (p. 751).

Iodine is readily soluble in alcohol, forming a brown solution known as **tincture of iodine** (½ oz. each of iodine, potassium iodide and water, and rectified spirit to 1 pint). The depression of freezing point of methylene iodide, CH_2I_2, containing dissolved iodine, gives the formula I_2.

Solutions of iodine in carbon disulphide are violet, the same colour as the vapour. In benzene and chloroform reddish-purple solutions are

formed. It is supposed that in these solutions mainly I_2 molecules are present The purple solutions in petrol show colloidal particles in a beam of light, and these particles are formed in solutions in toluene on exposure to light

In water, alcohol, ether and aqueous potassium iodide solution, iodine forms brown solutions A purple solution in chloroform becomes brown on addition of alcohol, but the original colour is restored on dissolving out the alcohol by shaking with water The purple solution in petrol becomes brown when cooled in solid carbon dioxide and ether, but the colour of the solution in carbon disulphide is unchanged. The brown solutions in alcohol and in aqueous potassium iodide show colloidal particles in a beam of light They contain complex ions, I_3', or associations of iodine with solvent molecules

Iodine combines directly with many elements, such as phosphorus and mercury, forming **iodides**

Test for iodine.—Solutions of iodine give a beautiful blue colour with starch-paste. The latter is prepared by warming "soluble starch" with water, or adding boiling water to ordinary starch made into a paste with cold water. 1 part of iodine in 5,000,000 parts of water may be detected by this reaction. The blue colour disappears on heating, but reappears on cooling.

EXPT 9.—Add a drop of a solution of iodine in potassium iodide to some potato starch solution in a test-tube. Heat the tube containing the blue liquid in a beaker of boiling water. the liquid becomes pale yellow or nearly colourless Cool the lower part of the tube in a beaker of cold water this part of the liquid 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.—Hydrogen and iodine combine only feebly: the affinity for hydrogen diminishes very rapidly in the series of halogens: F, Cl, Br, I A mixture of iodine vapour and hydrogen passed over heated spongy platinum forms hydrogen iodide, or hydriodic acid, 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 some of the sulphuric acid is reduced. Since hydrogen iodide is a more powerful reducing agent than hydrogen bromide, the

sulphuric acid is reduced not only to sulphur dioxide but also to sulphur and hydrogen sulphide :

$$H_2SO_4 + 2HI = SO_2 + I_2 + 2H_2O ;$$
$$H_2SO_4 + 6HI = S + 3I_2 + 4H_2O ;$$
$$H_2SO_4 + 8HI = H_2S + 4H_2O + 4I_2.$$

The usual method of preparation of hydrogen iodide gas 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.

EXPT. 10 —Four gm of red phosphorus and 20 gm. of iodine are shaken together in a flask, and about 15 c c of water slowly dropped on the mixture from a tap-funnel The evolution of gas may become very rapid, and the flask is then cooled. The gas is collected directly by displacement It is very soluble in water, and attacks mercury.

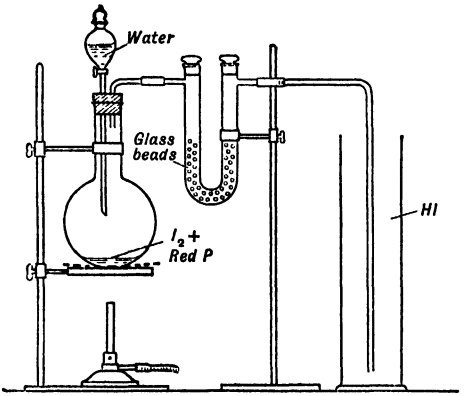


FIG 172 —Preparation of hydrogen iodide

Another method of obtaining the gas is to heat a mixture of iodine with colophonium resin.

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 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°	Critical pressure 82 atm.
Melting point −50·9°.	Relative density (H = 1) 63·94
Critical temperature 151°.	(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.

Dry hydrogen iodide mixed with dry oxygen is decomposed on exposure to light, with liberation of iodine : $4HI + O_2 = 2H_2O + 2I_2$. According to Berthelot, a mixture of 4 vols. of HI and 1 vol. of O_2 burns with a red flame when ignited.

Hydrogen iodide is decomposed by exposure to sunlight: after ten days Victor Meyer found 60 per cent. decomposed; after a year, 99 per cent. This photochemical decomposition occurs according to the equation: $HI \rightleftharpoons H + I$. 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 · $2HI \rightleftharpoons H_2 + I_2$ *The same equilibrium state is attained at a given temperature from the mixture of hydrogen and iodine vapour* ($H_2 + I_2$) *as from hydrogen iodide* (2HI). The catalyst produces no change in the composition of the equilibrium mixture, since it accelerates equally both the direct and inverse reactions. The equilibrium percentage dissociations of HI (Bodenstein) are:

$t°$ C. - - - - -	283°	356°	444°	527°
% dissociation of HI -	17·9	19·5	22·0	24·7

Aqueous hydriodic acid is produced by dissolving the gas in water. The apparatus shown in Fig. 169 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 hydrates $HI,2H_2O$, m pt. −43°, $HI,3H_2O$, m. pt −48°, and $HI,4H_2O$, m pt −36 5°, separate on cooling The solution ordinarily used in organic chemistry has a sp gr 1·5 An acid of maximum boiling point 126° 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 $4HI + O_2 = 2H_2O + 2I_2$ The ease with which this reaction occurs renders the concentrated aqueous acid a valuable reducing agent. It may be freed from iodine by distillation over a little red phosphorus

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 hydrogen sulphide through a saturated solution of iodine in water ·

$$H_2S + I_2 = 2HI + S.$$

When the liquid is decolourised it is again saturated with iodine, and so on; finally the sulphur is filtered off When the density of the solution reaches 1·56, the action ceases. Hydrogen sulphide gas reacts incompletely with dry iodine: the reaction is endothermic and reversible: $H_2S + I_2 = 2HI + S - 16·8$ k. cal.

The heat of solution of (HI) in a large quantity of water is 19·2 k. cal., hence heat is evolved by the action of hydrogen sulphide on iodine in presence of water.

Although the heat of formation of hydrogen iodide from hydrogen and *solid* iodine is attended with an absorption of heat

$$(H_2) + [I_2] = 2(HI) - 12 \text{ k cal}$$

the reaction $(H_2) + (I_2) = 2(HI)$ 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, in accordance with Le Chatelier's principle

Iodides.—Iodides may be prepared by the same general methods as bromides (*q v*) Nearly all iodides are soluble in water, cuprous, mercuric, lead and silver iodides being some exceptions Silver iodide forms a light yellow precipitate, insoluble in dilute nitric acid and in ammonia The formation of a violet vapour of free iodine when an iodide is heated with concentrated sulphuric acid and manganese dioxide; or a brown solution after addition of chlorine water, extracted by shaking with chloroform or carbon disulphide as a violet solution, may be used as tests for iodides

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 ·

$$5ICl + 3H_2O = 5HCl + 2I_2 + HIO_3 \text{ (iodic acid)};$$

it dissolves in concentrated hydrochloric acid without deposition of iodine, 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 of the solid is complete at 67°. It may be fused in chlorine under 16 atm. pressure. 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. 11.—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, often attended by a red flame, 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—**iodine monochloride**, ICl, (iii) lemon-yellow crystals in the lower jar—**iodine trichloride**, ICl_3. The reaction is

$$4HI + 4Cl_2 = 4HCl + I_2 + ICl + ICl_3$$

On standing in presence of excess of chlorine, only yellow crystals of ICl_3 remain.

Iodine trichloride may be regarded as a *salt* corresponding with the (unknown) basic oxide I_2O_3, **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 described. The latter said to be 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 **orthophosphate**, IPO_4, is said to be formed from iodine, orthophosphoric acid, acetic anhydride and fuming nitric acid. The strongly basic **diphenyliodonium hydroxide** $(C_6H_5)_2IOH$, is stable, and forms salts which resemble those of tervalent thallium, even to giving a green flame reaction.

Iodine monobromide, IBr, is formed by direct combination as black crystals similar to iodine, m. pt. 36°, b. pt. 116°. The vapour is dissociated.

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 formulae are known.

The best-known oxide of iodine is the pentoxide, but two lower oxides, I_4O_9 and IO_2 have been described.

A yellow oxide, I_4O_9, 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 I_2 and I_2O_5 at 180°.

Iodine pentoxide, or **iodic anhydride**, I_2O_5, is obtained by heating iodic acid to 200°, or at 150° for three hours and then at 240° in a current of dry air: $2HIO_3 = H_2O + I_2O_5$. It is a white powder, 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, of which it is the anhydride.

Hypoiodous acid.—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 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: $I_2 + H_2O \rightleftharpoons HI + HOI$, or $I_2 + 2OH' = I' + OI' + H_2O$. The existence of a lower oxy-acid of iodine in the freshly-prepared solution of iodine in alkali may be inferred from the colour and smell, and its oxidising and bleaching properties. Indigo solution is bleached, hydrogen peroxide evolves oxygen, manganous sulphate is precipitated as brown manganic hydroxide, and if alcohol is added to the solution a yellow precipitate of iodoform, CHI_3, is obtained.

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 formed on shaking an aqueous solution of iodine with precipitated mercuric oxide:

$$2HgO + 2I_2 + H_2O = HgI_2,HgO + 2HOI.$$

The acid appears to have an amphoteric character, functioning as a very weak base as well as a very weak acid:

$$HO' + I^{\cdot} \rightleftharpoons HOI \rightleftharpoons H^{\cdot} + OI'.$$

Iodic acid.—This, the most important oxy-acid of iodine, is formed by the oxidation of iodine with ozone in presence of water, or by boiling iodine with ten times its weight of nitric acid (sp. gr. 1·5) in a flask, 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.

Iodic acid is 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 addition of silver oxide, when insoluble silver chloride is formed.

Iodic acid may also be prepared by adding iodine to a hot concentrated solution of potassium chlorate, and warming with a few drops of nitric acid: $5KClO_3 + 3I_2 + 3H_2O = 6HIO_3 + 5KCl$, or by evaporating iodine with 25 per cent. chloric acid.

Iodic acid is insoluble in alcohol; it is very soluble in water, but is not deliquescent. The solution first reddens and then bleaches

litmus paper. The solid deflagrates when heated with powdered charcoal, sulphur, phosphorus, or organic matter, and is an oxidising agent:

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

Iodic acid melts at 110° to form a solution and a solid hydrate of I_2O_5, viz., $3I_2O_5,H_2O$, which is stable to 196°, but then fuses again and forms I_2O_5.

If iodine is dissolved in aqueous alkali, an **iodate** and iodide are formed: $3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O$ (Davy, 1813). If an acid is now added, the whole of the iodine is set free again, on account of the reduction of the iodic acid by the hydriodic acid. An acid may be estimated by adding it to a neutral solution of iodide and iodate, and titrating the iodine liberated.

On adding iodine to a hot concentrated solution of potash, **potassium iodate**, KIO_3, crystallises out on cooling, as it is sparingly soluble. 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, although a monobasic 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 $KH(IO_3)_2$;
Diacid potassium iodate, $KIO_3,2HIO_3$, or $KH_2(IO_3)_3$.

The acid salts are isomorphous with acid salts of some dibasic organic acids (succinic, etc.). The normal iodates are sparingly soluble or insoluble in water. On heating, they break up in one of two ways: (i) into iodide + oxygen, *e.g.*, KIO_3; (ii) into oxide + iodine + oxygen, *e.g.*, $Ca(IO_3)_2$. Barium iodate forms a periodate (see below). Iodates form complex compounds with molybdic, tungstic, selenic, sulphuric and phosphoric acids.

Iodates are detected by the blue colour, due to liberation of iodine, produced when sulphurous acid and starch-paste are added to a solution.

The formula of iodic acid is assumed to be $HO—I\overset{O}{\underset{O}{\ll}}$, in which iodine is quinquevalent.

Periodic acid.—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 $HIO_4,2H_2O$. By heating in a vacuum at 100°, HIO_4 is said to be formed, but decomposition easily occurs, so that the formula of the hydrate 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.

Iodic acid is oxidised to periodic acid by permanganate and sulphuric acid.

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 12·7 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 suspension of this salt in water gives with silver nitrate at 100° 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, which is evaporated on a water-bath and crystallised by standing over sulphuric 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 may be regarded as 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.*, $Ba_5(IO_6)_2$.

FLUORINE.

Occurrence of fluorine.—The mineral *fluorite*, or *fluorspar*, occurs in Derbyshire, crystallised in cubes or octahedra (Fig. 173), or in compact masses like marble. It is known as "Derbyshire Spar," or when the crystals are 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**. 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*)

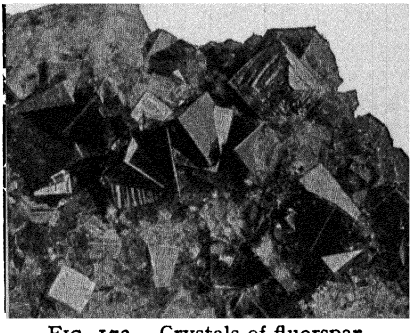


FIG. 173.—Crystals of fluorspar.

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.

The composition of fluorspar was for long unknown. It appears that crude hydrofluoric acid was first prepared by an unknown English glass-worker about 1720 Priestley, and in 1771, Scheele, discovered that fluorspar was a salt of lime and a peculiar acid, which Scheele obtained in an impure state by distilling fluorspar with concentrated sulphuric acid in a glass retort The retort was powerfully corroded, and a gas formed which deposited gelatinous silica on passing into water J C F. Meyer (1781), and C. F Wenzel (1783), used iron and lead vessels and obtained fairly pure hydrofluoric acid in solution, the part played by the silica from glass being clearly recognised In 1786 Scheele used a tin retort in the preparation of the acid The use of metal vessels had been suggested, not tried, by Wiegleb in 1781, but with doubts as to its practicability. 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 chlorine. Fluorspar would then be calcium fluoride, CaF_2. The element was first isolated by Moissan in 1886.

Fluorine is widely distributed both as fluorspar and in other fluorides Large quantities of *cryolite*, a double fluoride of sodium and aluminium, $AlF_3,3NaF$, or Na_3AlF_6, are found in Greenland, and *fluor-apatite*, $CaF_2,3Ca_3(PO_4)_2$, is common. 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 Wolsendorf, which have been decomposed by the radioactive uranium minerals found in the same localities, but the blue colour of some kinds of fluorspar is apparently due to organic matter On heating, it disappears. Colourless fluorspar becomes blue when exposed to radium emanation.

The isolation of fluorine.—The isolation of fluorine was for long one of the master problems of inorganic chemistry. The attempts of Davy, Fremy, Nicklès, Louyet, and Gore towards its solution were uniformly unsuccessful. If platinum vessels were used, a chocolate-coloured powder, PtF_4, was obtained; 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. Moissan in 1886 found that the anhy-

drous acid became an electrolyte when potassium hydrogen fluoride, KHF_2, was dissolved in it. If this solution is electrolysed in a U-tube composed of an alloy of platinum and iridium with electrodes of the same material, the whole being strongly cooled, hydrogen is evolved from the cathode and fluorine from the anode. In 1899 Moissan found that the platinum apparatus could be replaced by copper, which apparently becomes coated with a protecting film of fluoride. The electrodes must still be of platinum-iridium.

On the left in Fig. 174 is the U-tube, of 300 c.c. capacity, containing 60 gm. of acid potassium fluoride dissolved in 200 c.c. of anhydrous

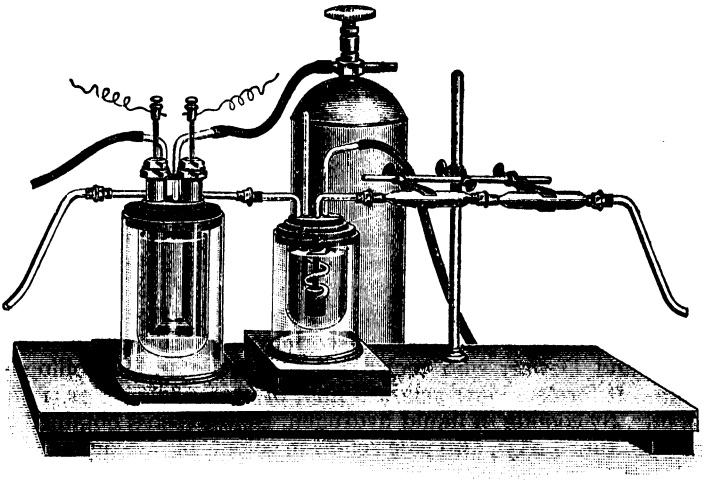


FIG. 174.—Moissan's apparatus for preparing fluorine.

hydrofluoric acid. The electrodes are insulated by stoppers of fluorspar, covered outside with shellac. The tube is immersed in a bath of methyl chloride, b. pt. $-23°$, which is constantly renewed, and a potential of 50 volts is applied. 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 from the cathode, and absorbing the fluorine in iron wire in a weighed platinum tube, Moissan found that for every gram of hydrogen evolved the iron increased in weight by 19 grams. The gas was therefore free fluorine. The electrolyte is probably potassium fluoride, the acid acting as an ionising solvent.

Fluorine is more easily prepared by the electrolysis of fused $NaHF_2$, or better KHF_2, in a copper vessel with graphite electrodes. The electrolyte, pure and dry KHF_2 (m. pt. 217°), is fused in an electrically

heated wide copper V-tube, *AA* (Fig 175); the electrodes, *RR*, are pure Acheson graphite rods insulated in bakelite cement stoppers, *BB*. A current of 5 amp. at 12 volts is used. The fluorine (0·92 litre per hour) is purified by passage through two copper U-tubes, *FG*, containing dry sodium fluoride (Dennis, Veeder and Rochow, 1931). Purity of the salt and of the electrodes is essential Brauner (1894) obtained small quantities of fluorine by heating potassium fluorplumbate,

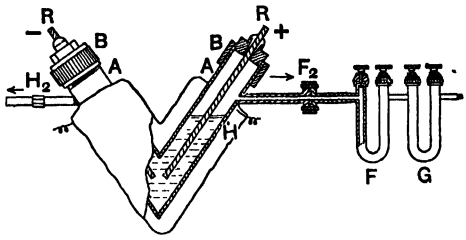


FIG. 175.—Preparation of fluorine

$$PbF_4,3KF,HF,$$

procured by the action of hydrofluoric acid on potassium plumbate. 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 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 18·91 (H = 1), from which the formula F_2 follows. Fluorine was liquefied in 1897 by Moissan and Dewar, who cooled the gas in liquid air boiling in a vacuum. It forms a clear yellow liquid, b. pt. −187°, sp. gr. 1·108 at the b. pt. 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. Fluorine is the most active element known; it does not react directly with oxygen or nitrogen, and combines with chlorine only on heating (p. 381). It readily combines with bromine and iodine, forming BrF_3 and IF_5, both colourless liquids.

Fluorine unites with moist hydrogen explosively even at −252°, but the very pure and dry gases do not react at room temperature (cf. p. 198); 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. Iron, zinc, tin, magnesium, manganese, nickel, aluminium, and silver take fire when gently warmed. Lead is only slowly attacked at the ordinary temperature, and copper becomes coated with a protective

layer of fluoride. 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 water, hydrofluoric acid and strongly ozonised oxygen are produced :

$$3H_2O + 3F_2 = 6HF + O_3.$$

Fluorine can replace oxygen in many acids without producing much change in chemical properties, *e.g.*, it forms fluoriodates, MF_2IO_2, and $IF_3(OH)_2$, and replaces oxygen in niobates and tantalates A mixture of fluorine and oxygen explodes when subjected to the silent discharge.

Hydrofluoric acid.—Hydrogen and fluorine combine when moist, forming hydrogen fluoride, or hydrofluoric acid, HF, which is more conveniently obtained by the action of sulphuric acid on fluorides, or by heating acid potassium fluoride

$$KHF_2 = KF + HF.$$

If powdered fluorspar is distilled with 90 per cent. sulphuric acid in a lead retort, connected with a lead receiver containing water, the vapour of hydrofluoric acid dissolves in the latter to form a colourless solution : $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. This is kept in wax or gutta-percha bottles, and is used for etching or engraving on glass. The latter consists of alkali and alkaline earth silicates ; hydrofluoric acid removes the silica in the form of silicon fluoride :

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

Etchings with the liquid acid are clear ; those made with the gas, or a mixture of aqueous acid and ammonium fluoride, are opaque.

EXPT. 12.—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 sand from castings, and as an antiseptic. The so-called " wild yeasts," which produce fusel oil in fermentation, are killed by small quantities of fluorides such as sodium fluoride, whilst normal yeast-cells may be accustomed to it. Lactic and butyric fermentations are also inhibited. 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 or copper

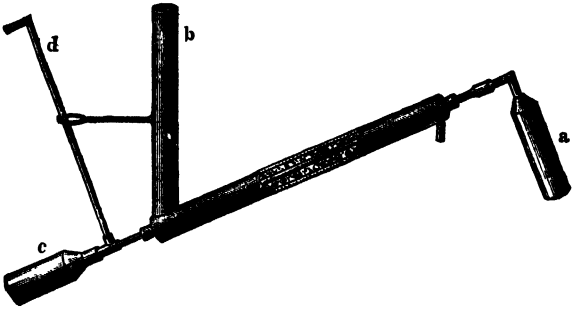


FIG 176.—Platinum retort and condenser for preparing anhydrous hydrofluoric acid

retort, connected with a condenser of the same metal cooled by a freezing mixture, **anhydrous hydrofluoric acid** distils over (Fig. 176). $KHF_2 = KF + HF$. The anhydrous acid, first prepared in this way by Fremy in 1856, may also be obtained by heating lead fluoride in hydrogen: $PbF_2 + H_2 = Pb + 2HF$.

Ammonium fluoride, NH_4F, obtained by neutralising the acid with ammonium carbonate, decomposes on fusion and forms the acid fluoride: $2NH_4F = NH_3 + NH_4HF_2$.

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° or −83°. When quite free from water the liquid acid is said not to attack glass or metals at the ordinary temperature, except potassium, which explodes in contact with it. According to Moissan, the dry *gas* attacks glass. 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. Ceresin wax, however, resists the concentrated acid, which is kept in bottles of it. The acid and its vapour are dangerous corrosive poisons. They attack the skin violently and form sores which heal only with great difficulty.

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. Simons and Hildebrand (1924) conclude from measurements of vapour pressure and density that the gaseous acid is a mixture of H_6F_6 and HF molecules in equilibrium, at temperatures of 15°–19° C.

In concentrated solutions the acid appears to be H_2F_2, but in dilute solutions, from freezing-point measurements it has the formula HF, and the existence of H_2F_2 molecules is doubtful

The **fluorides** differ in many respects from the other halogen compounds. Silver fluoride is very soluble, calcium fluoride is nearly insoluble, in water. 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 compounds with hydrofluoric acid: *e.g.*, HBF_4, H_2SiF_6, H_2NbOF_5, etc., which form salts, *e g.*, KBF_4, K_2NbOF_5.

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 k. cal., this being the heat evolved in the reaction: $H'Aq + OH'Aq = H_2O$. Hydrofluoric acid, however, on neutralisation evolves 16·3 k. cal, whilst if excess of the acid is added to the neutral salt, 0·3 k. cal. is *absorbed*. The conductivities of solutions of the acid show that it is much less ionised than the other halogen hydracids; in decinormal solutions the percentage ionisation of hydrofluoric acid is about 15. On neutralisation the un-ionised molecules break up into ions as the reaction $H' + OH' = H_2O$ proceeds, and the

abnormally large heat of neutralisation indicates that heat is *evolved* in the reaction: $HF \rightleftharpoons H^{\cdot} + F'$.

The weak acetic acid has a nearly normal heat of neutralisation, 13·3 k. cal.; hypochlorous acid has a very small heat of neutralisation, 9·8 k. 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 almost completely ionised in decinormal solution

Fluorine oxide.—In 1929 Lebeau and Damiens found that a gaseous oxide F_2O is produced by passing fluorine at the rate of 1 litre per hour through 2 per cent. caustic soda solution: $2F_2 + 2NaOH = 2NaF + F_2O + H_2O$. It may be collected over water and liquefied in liquid air, b pt. −146·5°, m. pt. −223 8°. It is a stable gas.

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 abs.	Boiling point abs.	Sp gr of liquid	Solubility in water gm /lit at 0°
F	19	gas	pale greenish-yellow	40°	86°	1·108	decomposes
Cl	35·5	gas	greenish-yellow (liquid yellow)	172·2°	238·6°	1·55	14·6
Br	80	liquid	dark red (vapour red)	265·9°	331 9°	3·19	41·5
I	127	solid	black (vapour violet)	386·6°	457·5°	4·9 solid	0·162

In a similar way, we may compare the *physical properties of the hydrogen compounds*, all of which are *acids*:

Compound	Melting point abs.	Boiling point abs.	Density of liquid	Heat of formation in k. cal	Atomic distance A U	Energy of formation from atoms k cal
HF	180·8°	292·5°	0·988/15°	38·5	·94	160
HCl	157·8°	188°	0·929/0°	22	1·28	100
HBr	185·0°	206°	2·16 (b pt)	12·1*	1·42	85
HI	222·2°	237·6°	2·80 (b pt.)	−6·1†	1 5	70

The physical properties of hydrofluoric acid are abnormal; it is *associated* even in the gaseous state below 80°, whereas the other substances

* From $\frac{1}{2}(Br_2)$ † From $\frac{1}{2}[I_2]$.

are normal. Polymerisation leads to an increase of boiling point The energies of formation from the free atoms diminish as the distances between the atoms increase.

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 1000°. The halogens also displace one another from their binary salts in the order of the heats of formation, viz.: $F \rightarrow Cl \rightarrow Br \rightarrow I$. In the oxygen compounds, however, iodine can displace chlorine.

Compounds of fluorine with other halogens.—**Chlorine monofluoride,** ClF, is a colourless gas (m.pt −161°, b.pt. −103°) formed from hydrogen fluoride and chlorine at liquid air temperature, or by heating fluorine and chlorine in a copper vessel at 250°. It reacts with some metals even more vigorously than fluorine itself. With excess of fluorine, **chlorine trifluoride,** ClF_3 (m.pt. −83°, b.pt. +11·3°) is produced, this attacks glass very vigorously.

Bromine trifluoride, BrF_3, is formed from fluorine and bromine or hydrogen bromide, as a colourless fuming liquid, m pt. −2°; the **pentafluoride,** BrF_5, is formed from the elements at 0°, m.pt. −61·3°, b pt. 40·5°, the vapour being stable at 460°.

A liquid **iodine pentafluoride,** IF_5 (m.pt. −8°, b.pt. 97°), is formed by direct combination of the elements, by the action of fluorine on heated I_2O_5, or (Gore, 1871) by heating iodine with silver fluoride When heated with fluorine at 270°-300° it forms the gaseous **iodine heptafluoride,** IF_7, with the normal vapour density.

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. 119).

The application of as many as possible of these methods 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 it could not alone have given a certain result since it could not be assumed that the compound contained only one atom of the element.

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 *g cal*

The temperatures of quantities of solid elements in the proportion of their atomic weights are therefore raised through 1° 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 the *mean* energy of a monatomic solid due to atomic vibration, is half kinetic and half potential (as in small vibrations), and that the *kinetic* energies of the atom of the solid and that of a monatomic gas are equal at the same temperature (Maxwell's **law of equipartition of energy**), Boltzmann (1871) showed that the atomic heat of the solid should be twice that of the monatomic gas, viz., $2 \times 3 = 6$ g. cal. (p. 228). The table on opposite page gives results determined near atmospheric temperature.

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 : except in one or two cases these modifications have been confirmed.

TABLE OF ATOMIC HEATS.

Element	Atomic weight	Specific heat (20° to 100°).	Atomic heat = Atomic weight × Specific heat.
Arsenic	74·96	0·0827	6·22
Bismuth	208·0	0·0303	6·30
Bromine (solid)	79·92	0·0705	5·63
Calcium	40·07	0·149	5 97
Cobalt	58 97	0·1030	6·03
Copper	63·57	0·0928	5 90
Gold	197 2	0·0316	6·23
Iodine	126·92	0·0524	6·64
Iron	55·84	0 1096	6·12
Lead	207·2	0 0309	6·41
Lithium	6·94	0 94	6 52
Magnesium	24·32	0 2492	6 06
Mercury (solid)	200·6	0 0335	6 72
Nickel	58 68	0 1084	6·36
Phosphorus (yellow)	31 04	0 1981	6·20
Platinum	195 2	0 0320	6·25
Silver	107 88	0 0560	6 04
Sulphur	32 06	0·1751	5 61
Tin	118·7	0 0556	6 62
Uranium	238·2	0·0280	6·67
Zinc	65 37	0 0944	6 17

Mean atomic heat = 6·22

The present **exceptions to Dulong and Petit's law**, which give atomic heats lower than 6·3, occur among elements of *low atomic weight and high melting point*. Thus, although sodium (at. wt. 23; m. pt. 97·6°) conforms to the law, the elements beryllium (m. pt. 1280°), boron (m. pt. over 2000°), carbon (m. pt over 3500°) and silicon (m. pt. 1420°), with atomic weights lower than 30, all have atomic heats considerably below 6·3.

Weber in 1875 found, however, 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 in 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, as is shown by the figures in the table and by the curves of Fig. 177. 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

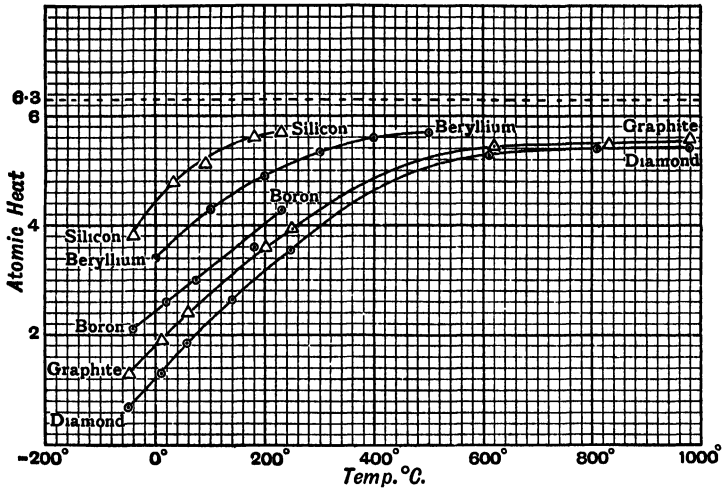


FIG 177 —Atomic heat curves

with abnormal atomic heats. The atomic heat of platinum in the interval 20°–1300° is 7·01 Those of lithium at −50°, 0°, 100° and 190° are 4·83, 5·22, 7·22 and 9·54 respectively.

Atomic heats at low temperatures.—The fact that the atomic heats of beryllium, boron, carbon, and silicon become larger and approach the normal values as the temperature rises, suggests that the atomic heats of elements which behave normally at ordinary temperatures might become abnormally small at low temperatures. This has been found by experiment to be the case. The atomic heats of *all* solid elements diminish to small values at low temperatures, some more rapidly than others, and at the absolute zero, −273°, the atomic heats are probably all zero. In the case of diamond, the atomic heat is actually zero at finite temperatures below −230°.

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 -	6·0	5·01	1·56
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 atomic heats of diamond 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 full curves of Fig. 178, from the experiments of Nernst.

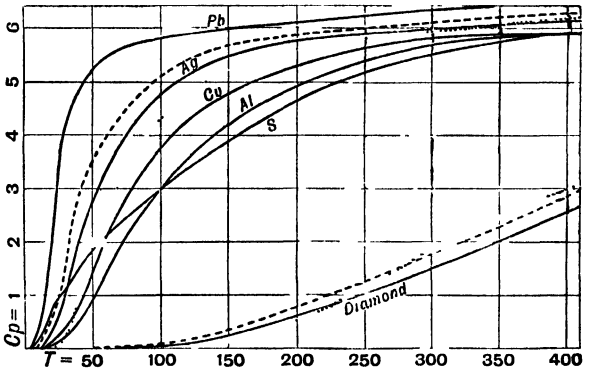


FIG 178 —Atomic heats at low temperatures

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 0500
22·31°	2·98	21 505°	0 1414
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 quantum theory of Planck (1900). According to this, the atoms of a solid do not take up heat energy continuously, but in finite quanta. 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 example, $\epsilon = h\nu = (6{\cdot}55 \times 10^{-27}) \times (2{\cdot}9 \times 10^{12}) = 1{\cdot}9 \times 10^{-14}$ ergs. (This value of ν is *not* the frequency of the light emitted by incandescent vapour but is the frequency of atomic vibration in the solid.)

The " deviations " from Dulong and Petit's law at low temperatures are explained by the theory ; the law is a limiting case of a more general

law. According this, the atomic heat of a monatomic solid element is given by the expression, due to Einstein (1907)

$$\text{Atomic heat} = 3R\frac{x^2e^x}{(e^x-1)^2},$$

where $x = h\nu/kT$, h being Planck's constant and k Boltzmann's constant, or the gas constant per *molecule*, $k = R/\mathbf{N}_0$, where R is the molar gas constant in absolute units and $\mathbf{N}_0$ Avogadro's constant (p. 225).

$$\therefore\ h/k = \frac{(6{\cdot}55 \times 10^{-27}) \times (6 \times 10^{23})}{8{\cdot}3 \times 10^{7}} = 4{\cdot}8 \times 10^{-11}$$

Planck's theory leads to the assumption of the atomic structure of radiation this is made up of quanta, $h\nu$, where ν is the frequency. The " critical energy " of a molecule (p 314) also appears to be of the form $h\nu$, where ν is some frequency characteristic of the substance.

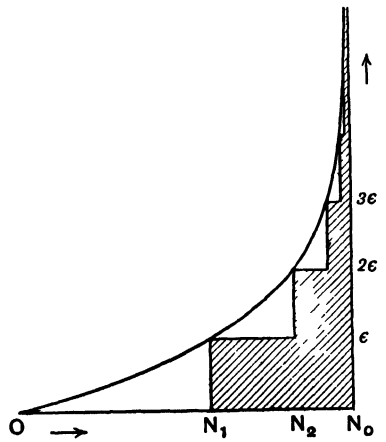


FIG. 179.—Energy distribution among aluminium atoms at 300° abs

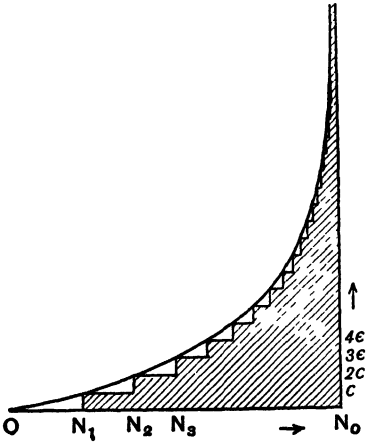


FIG 180.—Energy distribution among lead atoms at 300° abs.

According to Debye, the atomic heat of a solid at very low temperatures is proportional to the cube of the absolute temperature: At. ht $= aT^3$. This has been confirmed by Nernst and others.

It follows from the new theory that when ν (and therefore x) is very small and T is not too small, $e^x \to 1 + x$, hence $x^2e^x/(e^x-1)^2 \to 1$, or the atomic heat is $3R$, the value required by Dulong and Petit's law. The latter is therefore very approximately valid when the quantum is very small, *i.e.*, when the absorption of energy occurs very nearly continuously.

The increase of C_v above $3R$ at *high* temperatures is due to the fact that the amplitudes of the vibrations are then so large that the

simple harmonic vibration is departed from, and theory shows that in such a case $C_v = 3R + CT$ $(C > 0)$ Thus the curves when extrapolated to $T = 0$ should give the value 5·96 This has been confirmed for platinum and copper.

When the quantum is large there will be considerably less energy absorbed than would be the case if the absorption were continuous, and the atomic heat is abnormally low These results are shown graphically in Figs 179 and 180, in which the ordinates give the number of quanta absorbed and the abscissae, in which N_1 atoms out of a total of N_0 have no energy, $N_2 - N_1$ have one quantum (ϵ), $N_3 - N_2$ have two quanta (2ϵ), etc , are such that the area under the curve is proportional to the energy content The continuous curve represents the result for continuous absorption (total area $= 3RT$, Dulong and Petit's law) It is seen that the shaded area (quantum absorption) makes up only a small fraction of that under the continuous curve when the quantum is large (aluminium) but very nearly this area when the quantum is small (lead). This result is in agreement with the figures in the table on p. 384.

Atomic weights from specific heats.—Dulong and Petit's law gives an *approximate* value of the atomic weight of a solid element :

$$\text{Atomic weight} = 6{\cdot}3 \div \text{Specific heat.}$$

A volatile chloride of uranium has the following percentage composition : uranium, 62·66 ; chlorine, 37·34.

The equivalent of uranium, the weight combining with 35·5 parts of chlorine, is $62{\cdot}66 \times 35{\cdot}5/37{\cdot}34 = 59{\cdot}55$ The vapour density of the chloride was found by Zimmermann to be 191, hence the *approximate* molecular weight is $191 \times 2 = 382$ This will contain $37{\cdot}34 \times 382/100 = 142{\cdot}5$ parts, nearly equal to $4 \times 35{\cdot}5 = 142$ 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* $382 - 142{\cdot}5 = 239{\cdot}5$, nearly equal to $4 \times 59{\cdot}55 = 238{\cdot}2$, *i.e.*, four times the *accurately* determined equivalent. Thus, $U_x = 238{\cdot}2$. It has still to be decided whether this is the atomic weight of uranium, or a multiple of it. Thus, the following formulae of the chloride are possible :

Formula	At wt of Uranium.
UCl_4	238·2
U_2Cl_4	119·1
U_3Cl_4	79·4
U_4Cl_4	59·55

To decide which is the correct formula, an *approximate* value of the atomic weight of uranium must be found. The specific heat of solid metallic uranium is 0·0280 ; hence, by Dulong and Petit's law, the

atomic weight is *approximately* 6·3/0·0280 = 225. This shows that the *exact* value is 238·2, and hence the formula of the chloride is UCl_4.

It must be carefully noted that 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

Molecular heat of a compound.—An extension of Dulong and Petit's law was made by F Neumann in 1831, who found that *the specific heats of solid compounds 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 specific heat multiplied by the molecular weight : Neumann's law shows that the molecular heats of *similar* compounds are equal. The molecular heats of the carbonates of the alkaline-earth metals, etc., of the general formula RCO_3, are approximately 20 ; the sulphates, RSO_4, of the same metals have a molecular heat of about 25.

The relation between Neumann's and Dulong and Petit's laws 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. The heat content of a solid resides in its *atoms.* With gases, the case is quite different, since the kinetic energy of the *molecule* is predominant.

The molecular heat of lead iodide may be calculated from the sum of the atomic heat of lead and twice the atomic heat of the halogen. $PbI_2 = 6·41 + 2 \times 6·64 = 19\ 69$

The observed value is : (Pb + 2I) × sp. ht. of lead iodide = (207 + 2 × 127) × 0·0427 = 19 68.

Joule's law gives the atomic heats of elements in the solid state in cases where these cannot be directly determined.

Specific heat of silver chloride = 0·091 ; ∴ molecular heat of AgCl = 0·091 × (108 + 35·5) = 13·01 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

= 13 01 − 6·04 = 6·97

From the molecular heats of compounds, Kopp deduced the following atomic heats .

Boron - - -	2·7	Phosphorus - - -	5·4
Carbon - - -	1·8	Sulphur - - -	5·4
Silicon - - -	3 8	Oxygen - - -	4·0

These agree with the directly determined values at 0°–100°, although they are all abnormal. The abnormal atomic heats are therefore preserved in combination.

CRYSTALLOGRAPHY.

Crystals.—A distinction is usually drawn between **crystalline** and **amorphous** substances The most obvious difference is that of *external form*: amorphous solids are found in irregularly-shaped pieces; crystals usually have definite shapes Another difference is in the *fracture*: crystals break into 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 interposed 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. 181). $CaSO_4,2H_2O = CaSO_4 + 2H_2O$. 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

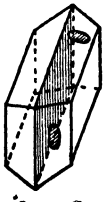


FIG 181.—Gypsum crystal showing plane of symmetry

We thus are able to recognise some definite **internal structure** in the crystal, which determines the outer form. Even if the outer form is destroyed by powdering, the internal structure remains. If the above experiments are tried with a piece of glass, 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 behaves as an amorphous body. The internal structure is more important than the external form.

The internal structure of crystals is due to a definite, ordered arrangement of the atoms or molecules in the crystal: this arrangement can be detected by the effect of the crystal, even in powder form, on X-rays. The molecular structure is, in general, **symmetrical**—a definite pattern is repeated over and over again in definite directions in space, in the same way, for example, as the pattern of a wall-paper in two dimensions The internal symmetry of the arrangement of the atoms or molecules corresponds with an external symmetry of the crystal form.

Symmetry of crystals.—The symmetry of a crystal form is determined by regularities in the positions of the similar faces, edges, etc.

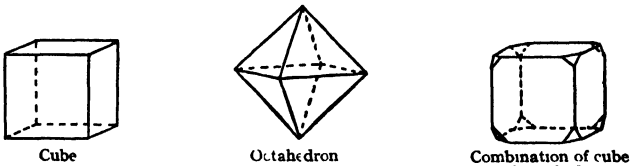


FIG 182

A crystal having all its faces alike is termed a **simple form**. both the **cube** and the **octahedron** in Fig. 182 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**: the crystal of galena shown in Fig. 182 is a combination of the cube and the octahedron; it contains sets of faces derived from each.

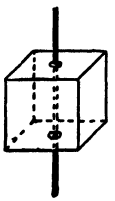


FIG 183 —Axis of symmetry of cube

The regularities in the positions of faces, edges, etc., 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. 181 into two similar and similarly-placed halves; this is the only plane of symmetry possessed by the gypsum crystal. An n-fold (or n-gonal) axis of symmetry is an axis such that, if the crystal is rotated around it, the crystal occupies the same position in space n times in a complete turn. The axis shown in Fig. 183 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°.

The crystal in Fig. 372 appears to have an axis of *two*-fold symmetry. But if the right-hand upper sloping face is rotated through 90° and then supposed reflected in a horizontal plane, we obtain the lower left-hand sloping face as a virtual image. This crystal is said to possess an *alternating axis of fourfold symmetry*

A **polar axis** is one such that the groupings of faces about its two ends are different. The two crystals in Fig 337 have polar axes

A crystal has a centre of symmetry when like faces are arranged in pairs in corresponding positions on opposite sides of a central point.

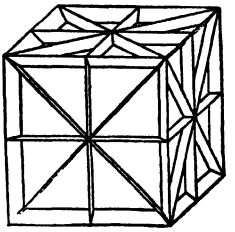


FIG 184.—Planes of symmetry of cube

An examination of a cube shows that it possesses 9 planes of symmetry (Fig 184), 13 axes of symmetry (3 of fourfold, 4 of threefold, and 6 of twofold symmetry), and a centre of symmetry It therefore possesses 23 **elements of symmetry**, 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 some have no element of symmetry at all.

The crystallographic symmetry depends on the internal 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 distorted crystals, and these angles are important in determining the crystal form. The angles between the faces of the perfect and distorted octahedra in Fig 185 are identical

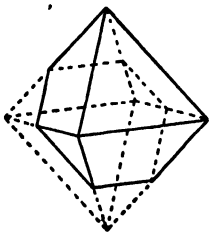


FIG 185.—Ideal and distorted octahedra, showing constancy of angles between the faces.

The **law of constant interfacial angles** was enunciated by Nicolas Steno in 1669 It is approximate, since slight differences in interfacial angle may occur in different crystals of the same substance

Crystallographic systems.—A simple method of classification of crystal forms is into crystal systems, 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 axes of symmetry.

The following six types of crystallographic axes are usually chosen :

1. *Three equal axes at right angles* : this corresponds with the **cubic, or regular,** system.

Fig 191 I. shows the **regular octahedron,** which is the typical **pyramid form** of the regular system, and the **cube,** which is the typical **prism form.**

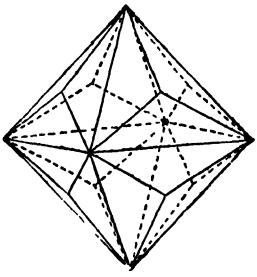


Fig 186 —Triakisoctahedron (three-faced octahedron)

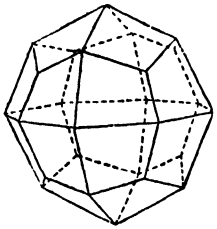


Fig. 187.—Icositetrahedron.

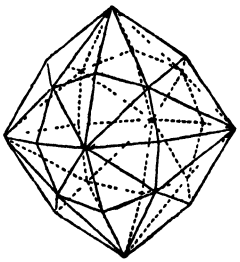


Fig. 188 —Hexakisoctahedron (six-faced octahedron).

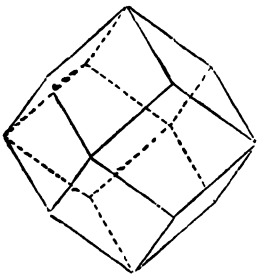


Fig 189 —Rhombdodecahedron

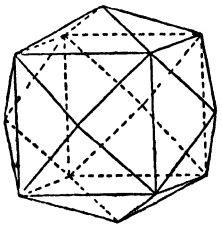


Fig. 190 —Tetrakis-hexahedron (four-faced cube)

The other simple forms of the system are the **triakisoctahedron** (Fig. 186), the **icositetrahedron** (Fig. 187), the **hexakisoctahedron** (Fig. 188), the **rhombdodecahedron** (Fig. 189), and the **tetrakis-hexahedron** (Fig. 190) Combinations of these forms also occur.

(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 Fig 191 II. There are two orders of pyramid and prism forms, according as the horizontal axes terminate at the angles or the middle point of the faces.

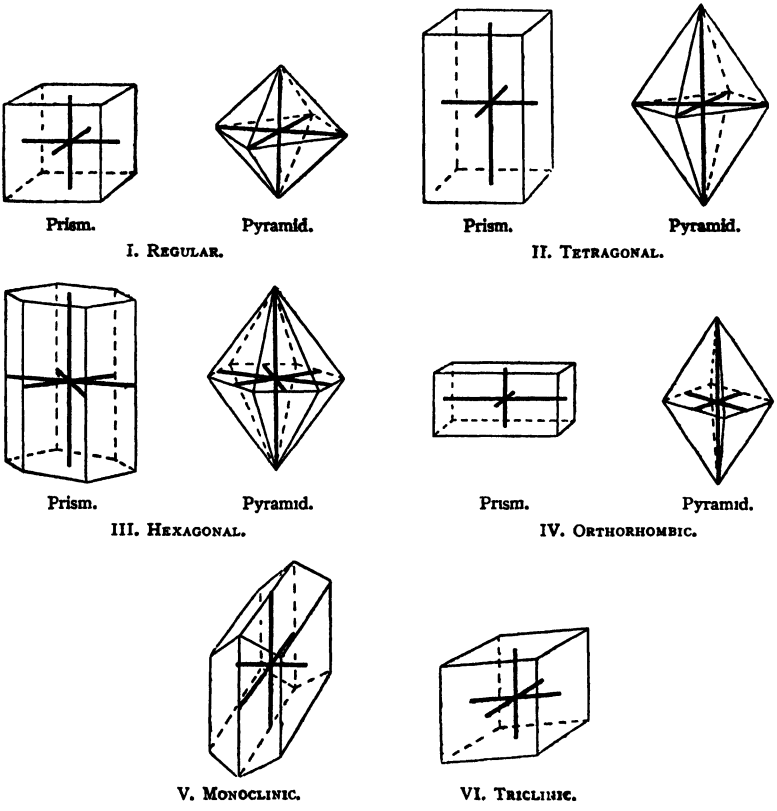


FIG 191 —Crystal systems.

If the length of the vertical axis is denoted by *c*, and the lengths of the horizontal axes by *a* and *b*, with appropriate signs, 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

Typical pyramid and prism forms are shown in Fig. 191 III.

(4) In the **orthorhombic 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.**

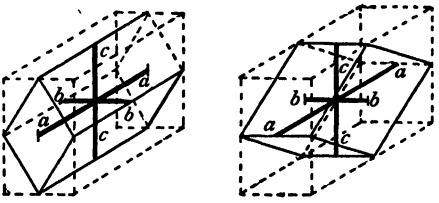


FIG 192.—Dome and pinakoid faces.

Pyramid and prism forms exist (Fig. 191 IV.), and 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 they are called **macrodomes**; if parallel to the shorter or brachy-axis they are called **brachydomes** (Fig 192)

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 Fig 192. In Fig 193, representing a crystal of barytes ($BaSO_4$), the faces marked 010 constitute a macropinakoid form, in this case a **basal pinakoid**; the faces 101 are the macrodome form The faces belonging to the prism form are marked 001, a notation explained later

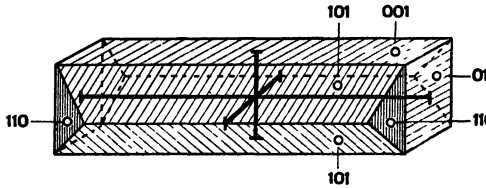


FIG 193.—Barytes crystal

(5) In the **monoclinic system** there are *three axes 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* (Fig. 191 V.). 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.

(6) In the **triclinic system** there are *three unequal axes intersecting one another obliquely* (Fig. 191 VI.) 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).

Most crystalline minerals belong to the monoclinic or rhombic systems; of 565 minerals listed by Beckenkamp, 186 were monoclinic, 155 rhombic, 85 regular, 51 rhombohedral, 36 triclinic, 32 tetragonal and 20 hexagonal.

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 the modern classification into symmetry groups, these are holohedral forms in separate classes.)

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. 194 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.

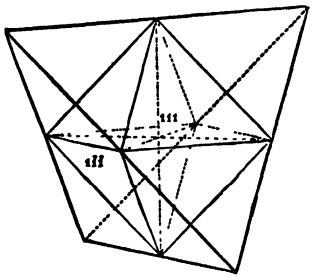


FIG 194 —Relation of tetrahedron (hemihedral form) to octahedron (holohedral form)

Important hemihedral forms occur in the hexagonal system. By developing alternate faces of the hexagonal pyramid (Fig. 195), one obtains the positive or the negative **rhombohedron** (Figs 196, 197) From the dihexagonal pyramid with 24 faces, obtained by the combination of

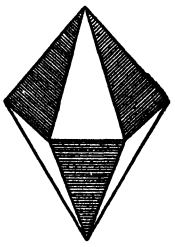


FIG 195

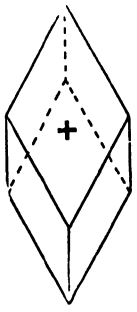


FIG 196

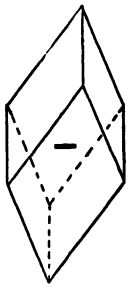


FIG 197

FIG 195 —Hexagonal pyramid · shaded faces to be suppressed

FIG 196 —Hemihedral form of hexagonal pyramid positive rhombohedron

FIG. 197.—Hemihedral form of hexagonal pyramid : negative rhombohedron

two hexagonal pyramids, two kinds of hemihedral forms are produced : (i) by suppressing alternate pairs of faces (Fig. 198) one obtains the

scalenohedron (Fig. 199); (ii) by suppressing alternate faces (Fig. 200) the **trapezohedron** (Fig. 201) results.

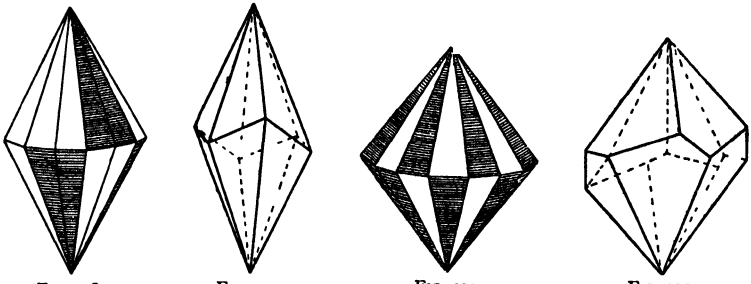
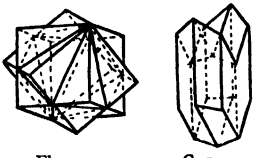


FIG 198 FIG 199 FIG 200. FIG 201

FIG 198.—Dihexagonal pyramid alternate pairs of faces to be suppressed
FIG 199.—Scalenohedron hemihedral form obtained from Fig 198
FIG 200.—Dihexagonal pyramid alternate faces to be suppressed
FIG 201.—Trapezohedron hemihedral form obtained from Fig 200

Twin crystals.—Two or more individual crystals sometimes grow in contact so that neither is complete, and **twin crystals** (Fig. 202) are formed. The two crystals may coalesce except for a few faces, as in Fig. 203



Fluorspar Gypsum

FIG 202.—Twin crystals

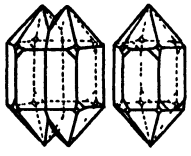


FIG 203.—Twins of right- and left-handed quartz
Partial and complete interpenetration

Crystallographic notation.—The form shown in Fig 204 contains two sets of faces, viz., the set *a*, *b*, *c* and the face *o*. Through the centre *O* draw axes *OX*, *OY*, *OZ* parallel to the faces as shown. These are the **crystallographic axes.** In the general case (for a triclinic crystal), they will be oblique axes, and the angles $YOZ = \alpha$, $XOZ = \beta$ and $XOY = \gamma$ will not be right angles. Each prism face cuts one axis only, since it is parallel to the other two, and the **intercepts** are the distances *a*, *b* and *c* from *O*. If we imagine the face *o* extended in all directions it will intercept all three axes. whatever the size of *o* its intercepts will remain in the same *ratio*. These ratios, generally denoted by $a : b : c$ for the

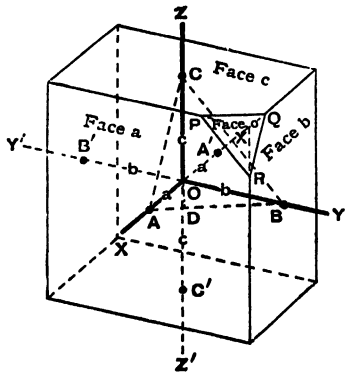


FIG. 204.—Crystallographic axes.

intercepts on the x, y and z axes, were called by Weiss (1818) the **parametral ratios**, the face o being the **parametral plane**. For the other pyramid facets the parametral ratios are $a : -b : c$, $a : b : -c$ and $a : -b \cdot -c$.

In *all* cases (whether the axes are rectangular or inclined) it is found that if o is an actual crystal face, the intercepts of *any other* actual face on the crystal can be expressed by the ratio $ma : nb \cdot oc$, where m, n, o are either small *rational* numbers or infinity For example, the prism face b makes intercepts $\infty a \cdot 1b \cdot \infty c$, since it is parallel to OX and OZ and its intercepts are infinite, whilst it cuts OY at a point which may be taken as the intercept of o also. This **law of rational intercepts** was implied in the attempts of Hauy since 1781 (Essai d'une Théorie sur la Structure des Crystaux, 1784), to show that derived forms may be produced by the decrements of successive layers of what he called *integrant molecules*, the form of which is that of the cleavage figure. The forms of rock-salt, for example, are produced by packing the hypothetical cubic integrant molecules together, and the development of an octahedral face is shown in Fig 205

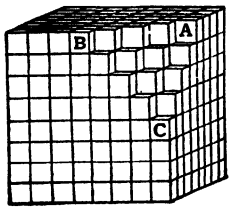


FIG 205.—Integrant molecules according to Hauy.

In the usual or **Miller system** of crystallographic notation (1839), the axial ratios a b c are first calculated from the facial angles as measured by a goniometer, the intercepts $\infty a \cdot 1b$ ∞c, for example, are then written $\frac{a}{\infty} \; \frac{b}{1} \; \frac{c}{\infty}$, and the denominators enclosed in a bracket are the **Miller indices** of the face (010) for the face b, and (111) for the face o. In the case of negative indices the sign is placed over the index : $(1\bar{1}1)$. As an example, consider the potassium dichromate triclinic crystal in Fig. 206. The edges selected for the directions of the three crystallographic axes OX, OY, OZ are the intersections of the faces B and C, C and A, and A and B, respectively. Hence the faces A, B and C will have the indices (100), (010) and (001) respectively The parametral face chosen, giving the basic ratio $a \cdot b \cdot c$, is p, and since it cuts the axis OZ at its negative end, its indices will be $(11\bar{1})$. The ratios $a : b : c$ and the angles α, β, γ between the axes ($\alpha = YOZ$; $\beta = XOZ$, $\gamma = XOY$) are calculated from the different angles which these four faces, A, B, C and p, make with one another, as read off on the goniometer. They are $a : b : c = 1{\cdot}0116 : 1 : 1{\cdot}8416$; $\alpha = 98° 0'$; $\beta = 96° 13'$; $\gamma = 90° 51'$. (It is customary to put the b axis ratio $= 1$.) The indices of the remaining faces are then found to be (as lettered in the figure) :

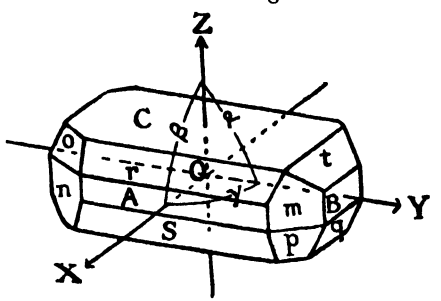


FIG 206.—Potassium dichromate crystals

$s(10\bar{1})$, $r(101)$, $m(110)$, $n(1\bar{1}0)$, $q(01\bar{1})$, $t(012)$, $o(1\bar{1}1)$, obeying the law of rational intercepts.

Brevais in 1848 replaced the idea of a packing of integrant molecules by an open structure in which the ultimate particles, which are considered as spheres, are arranged in a **lattice** (Fig. 207), of which he recognised 14 types. By considering the grouping of points in space lattices it has more recently been shown that there are 230 generalised types, such that the assemblage around any selected point is the same as, or the mirror-image of, the assemblage around any other point in the lattice. These 230 types may be allocated to classes according to symmetry. It is found mathematically that there are 31 possible combinations of the elements of symmetry in crystals obeying the law of rational intercepts, so that if we add the case where there are no elements of symmetry, we obtain 32 **symmetry groups.** Of these, eleven include nearly all the common crystalline substances. The question as to what particles occupy the lattice points can now be decided, in principle, by X-ray analysis.

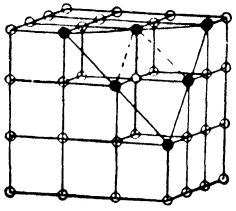


FIG. 207.—Space lattice of sodium chloride.

ISOMORPHISM.

Isomorphism.—The Abbé Haüy (1743–1822), the founder of crystallography, laid down as fundamental axioms that: (i) identity of crystalline form (except in the regular system) implies identity of chemical composition; and conversely (ii) difference in crystalline form implies difference in chemical composition.

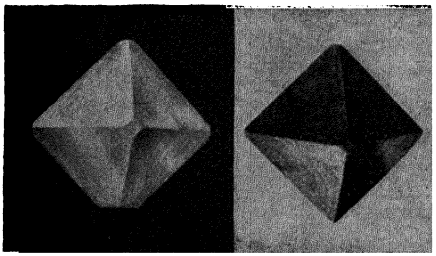


FIG. 208.—Crystals of common alum (left) and chrome alum (right).

Exceptions to these statements were, however, known. 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 have the same crystalline form, but differ in chemical composition (Fig. 208).

Mitscherlich (1819) showed that phosphates and arsenates of similar composition and containing 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. Hauy's first axiom seemed to be disproved. In the case of the salts $NaH_2PO_4 + H_2O$ and $NaH_2AsO_4 + H_2O$ the ordinary crystalline forms differ, but the phosphate sometimes crystallises in a 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. One substance may assume two distinct crystalline forms, and is then called **dimorphous**. If it assumes more than two forms it is called **polymorphous**. Hauy's second axiom, therefore, was disproved.

The capacity of different but chemically similar substances of crystallising in the same form, Mitscherlich called **isomorphism**; substances crystallising in the same form are **isomorphous**. Since numerous analogous compounds of phosphorus and arsenic, for example, are isomorphous, the name was applied to the elements themselves. **Isomorphous elements** form similarly crystallising compounds with the same elements or radicals: they can replace each other in their compounds without causing 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, no matter what the chemical nature of the atoms, the form being determined solely by their number and mode of combination. This generalisation was afterwards limited to the statement 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. In 1812, in fact, Wollaston had found with the reflecting goniometer that the corresponding angles in calcite, dolomite, and spathic iron ore are 74° 55′, 73° 45′, and 73° 0′. 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 Hauy's first axiom is therefore correct in the strictest sense, although it is often only by refined measurements that differences in the angles may be detected.

Tutton found that the crystal angles in isomorphous sulphates and selenates of potassium, rubidium, and caesium changed slightly when one isomorphous element (K, Rb, Cs, or S, Se) was replaced by another. The change, 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	$a : b : c = 0{\cdot}5727 : 1 : 0{\cdot}7418$
Rb_2SO_4	$a : b : c = 0{\cdot}5723 : 1 : 0{\cdot}7485$
Cs_2SO_4	$a : b : c = 0{\cdot}5712 : 1 : 0{\cdot}7531$
$(NH_4)_2SO_4$	$a : b : c = 0{\cdot}5635 : 1 : 0{\cdot}7319$

The other properties of the crystal (molecular volume, refractive indices, coefficients of expansion, thermal conductivity) alter with the crystal angles, showing that the crystalline form is closely related to the nature of the atoms in the crystal

Isomorphous elements.—It is possible to classify the elements into eleven groups, and the members of each group, capable of replacing one another without sensible alteration of crystalline form, 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 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. 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 $\overset{III}{Mn_2}O_3$, $\overset{III}{Fe_2}O_3$, etc), in group II because of the isomorphism of $\overset{VI}{K_2}MnO_4$ with $\overset{VI}{K_2}SO_4$, etc., and in group I because of the isomorphism of $\overset{VII}{K}MnO_4$ and $\overset{VII}{K}ClO_4$. The close connection between the valencies and the positions in the groups is clear.

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 formulae.*

Potassium selenate crystallises in the same form as potassium sulphate, hence Mitscherlich concluded that its formula is K_2SeO_4, corresponding with K_2SO_4. From its composition the atomic weight of selenium

could then be calculated. Ferric oxide, chromic oxide, and alumina are isomorphous; mineral crystals of them have the same form. The vapour density of aluminium chloride corresponds with the formula $AlCl_3$. The formula of alumina will then be Al_2O_3. We assume the formulae Fe_2O_3 for ferric oxide and Cr_2O_3 for chromic oxide, and from the compositions of the oxides the atomic weights of the metals may be calculated. These are confirmed by the specific heats, which are 0·1096 and 0·104 respectively.

A good example of isomorphism is that studied by Roscoe in connection with the atomic weight of vanadium The following minerals had the formulae given in the second column assigned to them by Berzelius

Apatite,	$3Ca_3(PO_4)_2 + CaF_2$	$3Ca_3(PO_4)_2 + CaF_2$
Pyromorphite,	$3Pb_3(PO_4)_2 + PbCl_2$	$3Pb_3(PO_4)_2 + PbCl_2$
Mimetesite	$3Pb_3(AsO_4)_2 + PbCl_2$	$3Pb_3(AsO_4)_2 + PbCl_2$.
Vanadinite,	$3Pb_3V_2O_6 + PbCl_2$	$3Pb_3(VO_4)_2 + PbCl_2$

In these formulae lead and calcium, and arsenic and phosphorus, replace each other, but the formula of vanadinite is different from those of the other compounds although the minerals crystallise in the same form Roscoe, therefore, concluded that Berzelius was in error in the formula of 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 formulae of the minerals, as shown in the third column, were then completely analogous. 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 $68·5 - 16 = 52·5$. Roscoe then found that the actual vanadium compounds investigated by Berzelius contained phosphoric acid, which is exceedingly difficult to separate By using pure compounds he found $V = 51·4$

Formulae of minerals.—Since one element can partly be replaced in a compound by an equivalent amount of an isomorphous element, the formula of the compound will not usually give a whole number of atoms of each isomorphous element. Spathic iron ore, $FeCO_3$, may have the iron partly or completely 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 The sum of the *atomic* proportions of Fe and Mn, combined with the group CO_3, must always be equal to unity.

Mixed crystals.—Isomorphous substances in many cases crystallise together from solutions to form *homogeneous* crystals containing them in variable proportions. These are usually known as **mixed crystals**; a more appropriate name is **solid solutions.** These are also formed from a fused state.

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, with colours varying from pale to deep purple according to the amount of chrome alum Isomorphous compounds cannot be separated in a state of purity by crystallisation 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) considered the property of forming mixed crystals a very important criterion of isomorphism, also 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. 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 The substances may be only partly miscible, in which case there is a gap in the line, but if they are isomorphous one part of the line is a continuation of the other

There are many exceptions to Retgers' theory Potassium and sodium chlorides, which crystallise in the same form and have identical lattices, do not form mixed crystals. The capacity for forming mixed crystals seems, in fact, to depend on an approximate equality of the volumes of the structural units. Ammonium sulphate, $(NH_4)_2SO_4$, molecular volume (M V.) 74, mixes in all proportions with rubidium sulphate, Rb_2SO_4, M.V. 73, with potassium sulphate, K_2SO_4, M.V. 65, and caesium sulphate, Cs_2SO_4, M V. 85, whilst potassium and caesium sulphates are completely immiscible, although they are undoubtedly isomorphous

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.—Apparent exceptions to the law of isomorphism are frequent. In some cases this is 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.

$$NaH_2PO_4,H_2O \quad \text{and} \quad NaH_2AsO_4,H_2O$$

In many cases, however, isomorphism is observed with substances exhibiting chemical similarities but with different numbers of atoms in the molecule: 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. In other cases, compounds are isomorphous which have the same numbers of atoms in the molecule, but are not chemically analogous: calcium carbonate, $CaCO_3$, occurs in the same form (*calcite*) as sodium nitrate, $NaNO_3$, the compounds Mg_2SiO_4 and Al_2BeO_4 are isomorphous. Crystals of sodium nitrate will form parallel growths on calcite crystals, and the two salts appear to be truly isomorphous.

Other examples of this type of isomorphism 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, appears to be verified

These apparent exceptions to the law of isomorphism, of great interest to crystallography, have received an adequate explanation from the results of the X-ray investigations of crystals and the modern theory of atomic structure, as will be explained in Chapter XXV.

CHAPTER XXIV

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 things grouped according to one kind of likeness may be 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 not always sharply defined, but the following are usually accepted as the most important:

METALS are *electropositive elements*; they normally give *basic oxides*, but acidic oxides may be formed when the atom has higher valencies, *e.g.*, $\overset{II}{Mn}=O$ (*basic*), $K-O-\overset{VII}{Mn}(=O)_2=O$ (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, $Zn(OK)_2$, with caustic potash, and is a type of an **amphoteric oxide**); their *halogen compounds* are *decomposed by water* almost completely · $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$; carbon tetrachloride and tetrabromide are exceptions, as they are not decomposed by water.

Certain physical properties commonly supposed to be characteristic of metals are subject to exceptions :

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, *e g*, bismuth, are relatively poor conductors.

The classification of elements according to **valency** is not entirely satisfactory, since : (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 and chlorine is a strongly electronegative non-metal, yet both are univalent elements.

The most satisfactory system of classification and the one now adopted, was based in the first instance on the relation between the properties of the elements and their **atomic weights.**

As early as 1817 Dobereiner noticed regularities in the atomic weights of chemically analogous elements. In groups of three, the atomic weight of the middle element is approximately the mean of the atomic weights of the extreme elements (**law of triads**) :

$$81 \begin{cases} \text{Cl } 35{\cdot}5 \\ \\ \text{I } 127 \end{cases} \quad \text{Br } 80 ; \qquad 80 \begin{cases} \text{S } 32 \\ \\ \text{Te } 128 \end{cases} \quad \text{Se } 79 ;$$

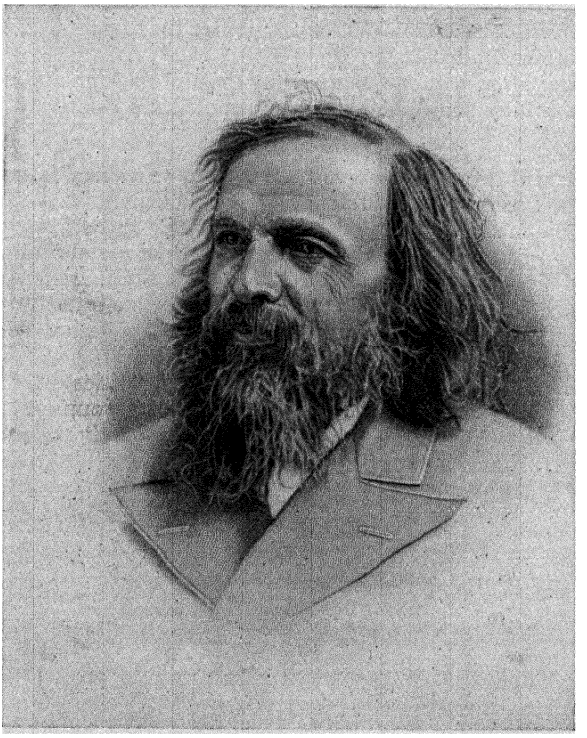
$$88 \begin{cases} \text{Ca } 40 \\ \\ \text{Ba } 137 \end{cases} \quad \text{Sr } 88$$

Similar regularities were pointed out by Gladstone, Cooke, Pettenkofer, Odling, and Dumas, but little progress could be 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 varying "equivalents," deduced from arbitrary considerations, continued to be used by different chemists, no regularities could ever come to light.

The periodic law.—Newlands, beginning in 1863, published a series of papers in the *Chemical News* in which he observed that *if the elements are arranged in the order of the (new) 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 are now called the **atomic numbers** of the elements, was not wholly satisfactory as can be seen. It was, therefore, coolly received by the Chemical Society in London, which declined to publish Newlands's paper in its journal.



MENDELÉEFF

Although the germ of one of the most important chemical laws is contained in Newlands's table, the credit of having stated clearly the connection between the properties of 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.

Mendeléeff's basic idea 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)

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. Immediately after the publication of this **Periodic Law** by Mendeléeff in 1869, an identical generalisation was put forward independently by Lothar Meyer in Germany 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 confirmed generally the changes boldly advocated by the Russian chemist.

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:

$$\text{Atomic volume} = \text{Atomic weight}/\text{Density} = A/D.$$

These atomic volumes represent, not the space occupied by the atoms themselves, but this plus the empty spaces between. If the atoms are assumed to be spherical and in contact, $\sqrt[3]{A/D}$ is a measure of the mean distance between the atomic centres

The atomic volumes of a few important elements are given below.

Element	Atomic volume at 15°	Element	Atomic volume at 15°
Hydrogen	13·2 at −250°	Strontium	34·5
Lithium	13·0	Barium	36·2
Sodium	23·7	Chlorine	20·6 (liq. at 0°)
Potassium	45·5	Bromine	25·4
Rubidium	56·25	Iodine	25·7
Caesium	70 6	Iron	7·10
Calcium	25·9	Lead	18·3

Mendeléeff remarked that reactive elements have large atomic volumes (alkali metals, 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. 209. 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 at low temperatures, heats of formation of oxides and chlorides, hardness, malleability, volatility, volume change on fusion, viscosity and colour of salts in aqueous

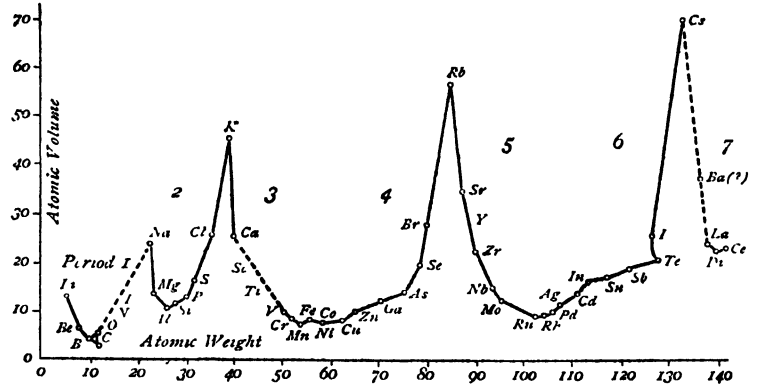


FIG 209.—Atomic volume curve

solution, mobilities of ions, electrode potentials of metals, over-voltage of metals, frequency of atomic vibrations in solids, distribution of the elements in nature, distribution of lines in spectra, 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). Gaseous elements and those fusing readily below a red heat (see table on p. 410), 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 is roughly defined by the chemical character of its oxide: **electropositive elements** yield *basic oxides*, 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.—It was formerly considered that the atomic heat was an exceptional property with respect to periodicity, since it is approximately constant the more accurate investigations of Dewar (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.

Compressibilities.—Since the compressibilities of solid elements are in periodic dependence on the atomic weights, T W. Richards supposed that this indicates that the atoms themselves are compressible 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. In general, compressibility increases with atomic volume

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, caesium).

"(3) The arrangement of the elements, or of groups of elements, in the order of their atomic weights, corresponds with their so-called *valencies*.

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
Aluminium	658 7	1800	Iodine	113 5	184 4	Rhodium	1970	> 2500
Antimony	630 5	1380	Iridium	2350 ?	> 4800	Rubidium	39 00	700
Argon	− 189 2	− 185 7	Iron	1533	3000	Ruthenium	2450 ?	> 2700
Arsenic	814 5 *	subl 615	Krypton	− 169	− 151 8	Samarium	1350	—
Barium	658	1810	Lanthanum	826	1800	Scandium	1200	2400
Beryllium	1350	1500	Lead	327 4	1620	Selenium(grey)	220	688
Bismuth	271	1450	Lithium	186	1609	Silicon	1420	2600
Boron	2300	2550	Magnesium	651	1380	Silver	960 5	1955
Bromine	− 7 2	58 8	Manganese	1260	1900	Sodium	97 90	882 9
Cadmium	320 9	767·3	Mercury	− 38 87	356 9	Strontium	752	1639
Caesium	28·45	670	Molybdenum	2620	3700	Sulphur	Sα 112 8 Sβ 118 95	444 55
Calcium	810	1712	Neodymium	840 ?	—			
Carbon	3500	4200	Neon	− 248 67	− 245 9	Tantalum	2850	> 4100
Cerium	640	1400	Nickel	1452	2900	Tellurium	452 5	1390
Chlorine	− 100 9	− 34 5	Niobium	1700	> 3300	Thallium	303 5	1650
Chromium	1805	> 2200	Nitrogen	− 210	− 195 8	Thorium	1845	> 3000
Copper	1083 0	2310	Osmium	2500 ?	> 5300	Tin	231·84	2260
Cobalt	1480	2900	Oxygen	− 218 4	− 183·0	Titanium	1800	> 3000
Fluorine	− 223	− 187	Palladium	1555	2200	Tungsten	3370	5900
Gallium	29 75	> 1600	Phosphorus	44 1	280 5	Uranium	< 1850	—
Germanium	958 5	2700	Platinum	1755	4300	Vanadium	1710	3000
Gold	1063 0	2610	Potassium	62 04	762	Xenon	− 140	− 109·1
Hafnium	1700	3200	Praseodymium	940	—	Yttrium	1490	2500
Helium	− 272 †	− 268 87	Radium	960	1140	Zinc	419 4	907
Hydrogen	− 259 14	− 252 76	Radon	− 71	− 61 8	Zirconium	1700	> 2900
Indium	155	> 1450						

* At 36 atm

† At 23 atm

"(4) The elements which are the most widely distributed in nature have *small* atomic weights, and . . . sharply defined properties. They are therefore typical elements.

"(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.]

"(8) Certain characteristic properties of the elements can be foretold from their atomic weights."

PERIODIC TABLE.

PERIOD	SERIES	GROUP I a	I b	II a	II b	III a	III b	IV a	IV b	V a	V b	VI a	VI b	VII a	VII b	VIII a	(0) b
1	1	H 1															He 2
2	2	Li 3		Be 4		B 5		C 6		N 7		O 8		F 9			Ne 10
3	3	Na 11		Mg 12		Al 13		Si 14		P 15		S 16		Cl 17			A 18
4	4	K 19		Ca 20		Sc 21		Ti 22		V 23		Cr 24		Mn 25		Fe 26 Co 27 Ni 28	
	5		Cu 29		Zn 30		Ga 31		Ge 32		As 33		Se 34		Br 35		Kr 36
5	6	Rb 37		Sr 38		Y 39		Zr 40		Nb 41		Mo 42		Ma 43		Ru 44 Rh 45 Pd 46	
	7		Ag 47		Cd 48		In 49		Sn 50		Sb 51		Te 52		I 53		Xe 54
6	8	Cs 55		Ba 56		15 Rare Earths 57–71		Hf 72		Ta 73		W 74		Re 75		Os 76 Ir 77 Pt 78	
	9		Au 79		Hg 80		Tl 81		Pb 82		Bi 83		Po 84		— 85		Em 86
7	10	— 87		Ra 88		Ac 89		Th 90		Pa 91		U 92					

The periodic system : Mendeléeff arranged the elements in a table, called the periodic table, or periodic system, a modern form of which is given above. In this the elements are arranged in nine vertical columns called **groups**, headed by zero (0) and the Roman numerals from I to VIII, or (as in the table given) the zero group is made a **sub-group** of VIII, each group being subdivided into *a* and *b* as shown.

These groups arise by suitably breaking up into **periods** a continuous series of the elements arranged in the order of their atomic weights. The ordinal numbers, called **atomic numbers**, are given in the table. If the periods are written one beneath the other in horizontal rows, the vertical columns constitute the groups. The first period contains two elements, hydrogen and helium; the next two periods contain eight elements each; elements of the third period are analogous to those vertically above them in the second period. In other words, the periodicity of properties begins again after neon, and the same types of properties are met with in the eleventh, etc., elements, as in the third, etc.

After argon, however, ten elements instead of eight must be passed over before the periodic recurrence of properties begins again with copper, and a close analogy, *e g* that between rubidium and potassium, only after eighteen elements At the beginning of this period we meet with a difficulty, 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, or VIII *b*, group The order of the two elements in respect of their atomic weights is, therefore, the reverse 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 common elements are known:

1. A 40; K 39. 2. Co 59; Ni 58·7. 3. Te 127·5; I 126 92;

and another case is believed to occur in the last period of radioactive elements, viz., protoactinum (Pa), 230, and thorium (Th), 232.

With this transposition of argon and potassium, the natural sequence runs along the period until manganese is reached We then expect an inert element resembling argon. Actually we find three elements, iron, cobalt, and nickel, with almost identical atomic weights and resembling one another very closely in 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 *a*, no representatives of which exist in the preceding periods. 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 or in *b* positions in the groups, whilst the other elements are placed on the left, or in *a* positions.

The three elements in Group VIII *a* 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 potassium to

krypton, inclusive, form 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 krypton by a second long period beginning with rubidium, followed by the even elements of the period as far as molybdenum. These elements resemble the corresponding even elements of the preceding long period. After molybdenum is the element masurium; then follows a cluster of three elements with very similar atomic weights and closely allied in physical and 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 *a*. The odd elements of the long period then follow, ending with xenon.

Near the end of this period 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 caesium and proceeds as far as lanthanum, in Group III, in a regular manner. After lanthanum, however, comes a series of fourteen elements with atomic weights differing by one, 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 fifteen elements now encountered:

La	Ce	Pr	Nd	Il	Sa	Eu	Gd	Tb	Dy	Ho	Er
138·9	140·13	140·92	144·3	—	150·4	152·0	157·3	159·2	162·5	163·5	167·14

Tm	Yb	Lu
169·4	173·5	175·0

In this case, instead of one element occupying one place in the group there seems to be a cluster of fifteen. These must be placed in the same group as scandium and yttrium; the regular 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 Then, after lutecium, the last of the rare-earth elements, comes an element discovered in zirconium minerals (alvite, malacon, etc.) by Coster and Hevesy in 1923, and named by them hafnium. It occupies the position in Group IV previously given to cerium, which must now be placed in Group III with the other rare-earth elements. After

hafnium come tantalum, tungsten, the element rhenium, and finally the three transitional elements: osmium, iridium, and platinum, which fall in Group VIII *a*. The rest of this long period is continued from gold in Group I, to bismuth in Group V, and the radioactive element polonium in Group VI. Element No 85, in Group VII is not known, and the period closes with the inert radioactive gas, the emanation, in Group VIII *b* (or Group O) This long period, therefore, contains in all 32 elements The numbers of elements in the periods up to this point are 2, 8, 8, 18, 18, and 32 (if we allow for one missing halogen element, No 85, in Group VII) A new period begins with radium, there being a missing element in Group I, and continues as far as uranium, all the elements in this group being strongly radioactive As far as is known uranium closes the periodic table, no element of higher atomic weight being known.

The close resemblance of elements occupying odd or even series and their difference from elements of even or odd series, respectively, in the same group, may be mentioned Thus, the even series in Group VI comprises Cr, Mo, W, U, and the odd 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) According to Paneth only those elements in a period which ends with an inert gas, *i e*, in the long periods only those in the odd series, can form *volatile* hydrides (*e g*, AsH_3, SbH_3, SnH_4, BiH_3) ; the hydrides of the elements of the other series (*e.g.*, LiH, NaH, KH, BaH_2) are salt-like solids

The periodicity of valency.—Mendeléeff pointed out that the number of the group corresponds with the valency of the elements occurring in it. In some cases (*e.g.*, N, S, Cl, Cr, Mn) 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 was urged as a defect of the periodic system by Wyruboff (1896) but the reason is now fairly clear from the point of view of atomic structure, as will be explained later. 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	(BeO_2)	B_2O_3	(CO_4)	N_2O_5	—	—	—
Na_2O	(MgO_2)	Al_2O_3	(SiO_4)	P_2O_5	(SO_6)	Cl_2O_7	—
K_2O	(CaO_2)	Sc_2O_3	(TiO_4)	V_2O_5	(CrO_6)	Mn_2O_7	—
Cu_2O	(ZnO_2)	Ga_2O_3	(GeO_4)	As_2O_5	$[SeO_6]$	—	—
Rb_2O	(SrO_2)	Y_2O_3	(ZrO_4)	Nb_2O_5	(MoO_6)	—	(RuO_8)
Ag_2O	(CdO_2)	In_2O_3	(SnO_4)	Sb_2O_5	(TeO_6)	$[IO_7]$	—
Cs_2O	(BaO_2)	La_2O_3	(CeO_4)	Ta_2O_5	(WO_6)	—	(OsO_8)
Au_2O	(HgO_2)	Tl_2O_3	(PbO_4)	Bi_2O_5	(UO_6)	—	—

The formulae of oxides enclosed in round brackets have been doubled; oxides in square brackets do not exist in the free state, but are known in compounds

The inactive gases, which form no compounds and have therefore zero valency, occupy the zero group or Group VIII *b*, separating the intensely electronegative elements of Group VII from the intensely electropositive elements of Group I. The transitional elements of Group VIII *a* 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 ·

$$\overset{-}{F}\ Ne\ \overset{+}{Na}\,,\ \overset{-}{Cl}\ A\ \overset{+}{K}\,,\ \overset{-}{Mn}\ (Fe,\ Co,\ Ni)\ \overset{+}{Cu}\,,\ \overset{-}{Br}\ Kr\ \overset{+}{Rb}\,;$$

$$\overset{-}{Ma}\ (Ru,\ Rh,\ Pd)\ \overset{+}{Ag}\,,\ \overset{-}{I}\ Xe\ \overset{+}{Cs}\,,\ \overset{-}{Re}\ (Os,\ Ir,\ Pt)\ \overset{+}{Au}.$$

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 noteworthy in 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 associate towards the left of the table, beginning with Group I; elements of strongly electronegative character occur on the right of the table, the most marked being in Group VII. In passing along a period from Group I to Group VII the electropositive character diminishes. When Group IV is reached the elements show very little 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 third 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. It is worthy of note that the non-metallic elements are confined to the upper right-hand part of the table.

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 the resemblances between Li and Mg, between Be and Al, and between B and C, are striking.

Differences between atomic weights.—The differences between the atomic weights of successive elements in the various periods show 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*, matter). In 1812 Davy had suggested that the " undecompounded substances " [elements] are compounds of hydrogen " with another principle as yet unknown in the separate form," and that " the same ponderable matter in different electrical states, or in different arrangements, may constitute substances chemically different "

Prout's hypothesis, although disproved in its original form by the accurate determinations of atomic weights made by Berzelius, 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 mistrust, which subsequent work did not justify. 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 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, so that small variations of composition of compounds might occur, which would explain the deviations from whole numbers. This contains the germ of the modern theory of isotopes. Stas, however, beginning with " an almost complete confidence in the exactness of the law of Prout," was led by his researches to conclude that it " is only an illusion, a pure hypothesis definitely contradicted by experiment " : it was also very definitely rejected by Mendeléeff.

Interest in Prout's hypothesis revived as a result of experiments by Crookes (1887) on the discharge of electricity through gases at very low pressure. Crookes was led to assume that 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. This was the beginning of the modern electrical theory of matter, which forms the subject of the following chapter.

Apart from hypothetical considerations, interesting regularities appear from an inspection of the periodic system itself.

Rydberg (1914) observed that the first short period contains $2 = 2.1^2$ elements, the two short periods, from Li to Ne, and from Na to A, contain each $2\ 2^2 = 8$ elements. The two long periods, from K to Kr, and Rb to Xe, contain each $2\ 3^2 = 18$ elements These should, if the same regularity holds good, be followed by two very long periods containing each $2\ 4^2 = 32$ elements, of which the first is known but only a fragment of the second exists, the table coming to an end with uranium. Bohr (1921) would write Rydberg's numbers as $2 = 1.2$, $8 = 2\ 4$; $18 = 3\ 6$, and $32 = 4\ 8$ Experiments on the scattering of X-rays by gases and modern atomic theory indicate consecutive positions for hydrogen and helium. Rydberg, however, considered that two hypothetical gases should come between H and He, and identified them with coronium and nebulium, evidence of the existence of which was supposed to have been found in the spectra of the sun and of nebulae. The existence of coronium (supposed by Nicholson to have an atomic weight 2·1) had been inferred from the bright green line 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 Coronium was reported in the spectrum of the nebula of Orion by Bourget, Fabry, and Buisson (1914). In the solar eclipse of 1914 the green line was hardly visible, but a new red line was very prominent Modern spectroscopy has disproved these interpretations, the peculiar lines are really due to common elements such as oxygen Mendeléeff regarded the ether as an inactive element of atomic weight about 10^{-6}, but the existence of the ether is no longer assumed in physical theories

Modern theories of atomic structure exclude the existence of atoms lighter than those of hydrogen, or with weights between those of hydrogen and helium, and it is believed that, apart from the elements number 85 and 87, the table is complete.

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 positions in the periodic table assigned to them by their chemical properties. Thus, **indium**, which occurs with zinc in minerals, has an equivalent of 38. From its occurrence with zinc the element was supposed to be bivalent, the oxide being InO, hence the atomic weight would be $38 \times 2 = 76$. 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 76 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 $38 \times 3 = 114$, 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 $6·3/0·055 = 114·5$. The element was then found to form alums, and therefore belongs to Group III

The element **beryllium**, with the equivalent 4·5, seemed to show resemblances to aluminium. The hydroxides of both 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 with potassium, dissolve in alkalies with liberation of hydrogen. The determination of the specific heat of beryllium, finally, gave 14·8 for the atomic weight. All these results appeared to show that beryllium was 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 magnesium, considering it to be bivalent and its oxide to be BeO. Its atomic weight should then be $4·5 \times 2 = 9·0$ 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 temperature, becoming 0·6206 at 500°: this gives Be = 9·8. Nilson and Pettersson (1884) 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 two 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 old atomic weight sequence. Chemical analogies in the periodic system strongly suggest the order: Os, Ir, Pt, Au, and more exact atomic weight determinations confirmed this.

Prediction of missing elements.—Mendeléeff in arranging the elements in the periodic system had to leave gaps in order that chemical analogies should be preserved. The next element known after calcium (Ca = 40) was titanium (Ti = 48). But titanium, if placed after calcium, would come in the third group under aluminium,

whereas its properties indicate that the element is quadrivalent and should 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 then a gap in the third group, between calcium and titanium Two similar gaps were also left in the next period Mendeléeff predicted that these three vacant places 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, but no chemist seems to have thought of doing this.

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 it with incandescence.
Element will be obtained by action of sodium on EsO_2, or K_2EsF_6.	Element obtained by reduction of GeO_2 by carbon, or of K_2GeF_6 by sodium.

EKASILICON (Es); predicted by Mendeléeff, 1871	GERMANIUM (Ge), discovered by Winkler, 1886.
Oxide EsO_2 will be refractory; sp. gr. 4·7; basic properties 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.
Hydroxide will be soluble in acids, but the 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. 86·5°, 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.

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 since been filled in by the discovery of the radioactive elements. The Periodic Law, therefore, pointed out the possibility of discovering new elements: it gave 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. In the later parts of the table, the question as to the possibility of new elements was far from clear, since the rare earths disturbed the order. Apart from these, however, the gaps corresponding with elements 43, 75, 84, 85 and 87 have always been recognised, and three of these have been filled, partly with the aid of information given by the ordinary periodic table in the same way as that which enabled Mendeléeff to predict the existence of scandium, gallium and germanium. Any suggestion that the Periodic System has been "superseded" by

modern theories is, of course, completely false, since it is the basis of the whole of our modern knowledge of atomic structure. What has happened is that the system has to some extent been *explained.*

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 Mendeléeff's periodic table.—The periodic classification in the form given to it by Mendeléeff was not free from difficulties and apparent contradictions. One of the most serious is the *inverted* positions of pairs of elements (A, K; Co, Ni; Te, I; Pa, Th). Again, it was very difficult to fit in the elements of the rare earth The transitional elements occupy an exceptional position; attempts to include them in the other groups were not successful.

The arrangement into groups overlooks some chemical analogies, such as those between boron and carbon, copper and mercury; and it also brings together elements which seem to 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. These regularities are explained to some extent by the modern theory of atomic structure, as will be seen later.

The most remarkable difficulty, however, is the position of hydrogen in the system. It may be omitted altogether, but usually shares a whole period with helium. If 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 will be gaps 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, forms salt-like hydrides such as NaH, and is a gas more difficult to liquefy than fluorine, yet the period should then contain unknown elements with atomic weights less than 1. However placed, hydrogen occupies an exceptional position: its best situation is probably at the head of Group I, on account of its more pronounced electropositive character.

CHAPTER XXV

THE STRUCTURE OF THE ATOM

The modern atomic theory.—The remarkable character of the Periodic System of the elements has given rise to a number of fundamental questions, some of which have received solutions only in recent years, when the structure of the atom has been revealed in ever increasing detail. Among the problems which present themselves are (1) the reason for the very approximately whole number atomic weights of some elements; (2) the explanation of the reversal of the order of atomic weights in the cases A, K; Te, I; Co, Ni; Pa, Th; (3) the reason for the occurrence of long and short periods and transitional elements, and the position of the elements of the rare earths. We desire also to know (4) what property of the atom really determines the position of an element in the Periodic System, since the order of the atomic weights is sometimes disturbed; (5) whether all the atoms are really composed of simpler constituents, and if so of how many; and (6) whether the atoms of one element are capable of being converted into those of another element.

The results of the experimental investigation of these problems constitute the modern atomic theory, and form the subject matter of the present chapter. Although, as will be seen, the fundamental researches in this field go back in some cases a considerable number of years, yet it is only since about 1910 that much progress has been made and many of the most important results have been obtained in a still more recent period.

Cathode rays.—Although the most familiar example of the production of free electrons is now their emission from the hot filament of the wireless valve, the recognition of the fundamental particle of electricity was the result of experiments on the **discharge of electricity in gases** at low pressures, first carefully studied by Faraday.

At a low pressure (0·01 mm.) an electrical discharge proceeds as a blue glow from the cathode in an 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 (Fig. 210). These cathode rays were discovered by Plücker in 1859; they are deflected by a magnet, showing that they are electrically charged. Perrin in 1895 was able to show 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 $1{\cdot}2 \times 10^8$ coulomb per gm ; recent determinations give $1{\cdot}772 \times 10^8$ cmb. per gm. The corresponding ratio for the hydrogen ion in electrolysis is $F = 96{\cdot}5 \times 10^3 / 1{\cdot}008 = 9{\cdot}58 \times 10^4$; the value for cathode rays is 1850 times this Of the two possibilities: (i) the charges the same, but the mass of the cathode particle 1/1850 that of the hydrogen atom; (ii) the masses the same, but the charge on the cathode particle 1850 that on the hydrogen ion, experiment decided in favour of the first. The cathode rays are free **negative electrons** They 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 from heated metals, by the action of ultra-violet light on metals, and in some chemical reactions This evidence points to electrons being *a common constituent of all atoms*

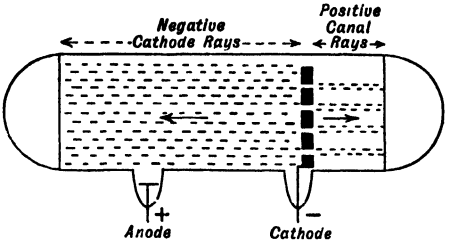


FIG 210 —Cathode and positive rays

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 The positive rays were investigated by Wien, by Sir J J Thomson, and later by F. W Aston Some of the particles were found to be uncharged

An electric discharge is passed through rarefied gas in a bulb. The cathode is an aluminium rod with a rounded end, pierced by a very fine copper tube, through which a fine pencil of rays passed through slits S_1S_2 (Fig. 211) between the plates P_1 and P_2, connected with the positive and negative poles of a battery, and then through a magnetic field at right angles to the electric field, this magnetic field passing between the poles of an electro-magnet shown in section at O. The rays are deflected by the combined electric and magnetic fields, and the separated pencils of rays then strike a photographic plate, GF. The rays characterised by definite values of mass to charge, m/e, are brought to a focus at F.

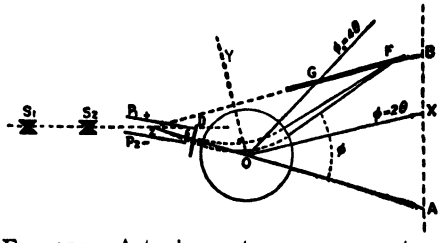


FIG. 211 —Aston's positive ray apparatus.

The particles are spread according to the values of m/e into a " mass spectrum," the foci of which are received on the plate, and since a narrow ribbon of rays was defined by the slits S_1S_2, these foci will be lines, each corresponding with a certain definite value of m/e. Some elements give lines indicating that they are mixtures of **isotopes.** Chlorine (35·46), for example, gives no line corresponding with its atomic weight but two lines indicating particles of masses 35 and 37. In the list of isotopes below, the numbers are in the order of intensities of the lines. In the case of mercury and hydrogen chloride, separation of the isotopes to a minute extent by distillation in a high vacuum and by diffusion, respectively, has been achieved.

TABLE I. ISOTOPES OF SOME ELEMENTS.

Element.	Atomic Weight.	Masses of Isotopes.
Hydrogen	1·008	1·0077 ; 2·014
Lithium	6·94	7 and 6
Boron	10 82	11 and 10
Carbon	12·01	12 and 13
Nitrogen	14·008	14 and 15
Oxygen (see p. 102)		16, 18 and 17
Neon	20·20	20 and 22 (21 ?)
Magnesium	24·32	24, 25, and 26 (Dempster)
Silicon	28·06	28, 29 and 30 (?)
Sulphur	32·06	32, 33 and 34
Chlorine	35 46	35 and 37
Argon	39·94	40 and 36
Potassium	39·10	39 and 41
Cobalt	58·94	59
Nickel	58·69	58 and 60
Bromine	79 92	79 and 81
Krypton	82·92	84, 86, 82, 83, 80, and 78
Rubidium	85·45	85 and 87
Tin	118·7	120, 118, 116, 119, 117, 124, 122, 121, 112, 114 and 115
Tellurium	127·59	130, 128, 126, and 125
Iodine	126·93	127
Xenon	130 2	129, 132, 131, 134, 136, 130, 128, 126, 124
Mercury	200·6	202, 200, 199, 201, 198, 204, 196

In some cases the method described is not applicable, *e.g.*, in the cases of metals or substances of small vapour pressure. Aston then made use of a second method, due to Gehrcke and Reichenheim, in which the anode consists of a heated strip of platinum foil with a depression

containing some of the salt of the metal, and placed opposite the cathode. By applying a high positive potential to the anode, positively charged metal atoms are given off as **anode rays**, which can be deflected in electric and magnetic fields as before. Another method was used by Dempster (1918), in which the positive ions emitted by heated metal salts in a high vacuum are allowed to pass through a potential difference, when they acquire equal energies After passing through a slit, the ions are then bent by a magnetic field into a semicircular path, so that they are just able to pass through a second slit into an electroscope. With a constant magnetic field, the potential difference required to cause the ions to pass through the fixed second slit is inversely proportional to m/e for the ion, the value of which is so determined.

It was at first thought that the masses of the isotopes were *exact* whole numbers, taking the mass of the oxygen atom as 16·00, hydrogen (H = 1·008) being the only exception. More refined measurements by Aston (1927) have shown that this is not the case, since the masses of the atoms of " simple " elements, *i.e.*, those having only one kind of atom, sometimes deviate from whole numbers by fractions which also appear in the " chemical " atomic weights, *e.g.*, N = 14 008, C = 12 0036 Since it is assumed that the atoms of all elements are formed from hydrogen nuclei (p 6) or protons, of mass 1 00778, and electrons of very small mass, the disappearance of the fractional mass in forming the atom is assumed to be due to the very large energy changes attending these hypothetical associations of protons and electrons, the energy change ΔE accompanying a mass change Δm according to Einstein's formula (p. 17) being $\Delta E = c^2 \Delta m$ A helium nucleus of mass 4·002 is formed from four protons of mass $4 \times 1{\cdot}0078 = 4{\cdot}0312$ and two electrons of mass $2 \times 0{\cdot}00054 = 0{\cdot}0018$ (O = 16·000) with a loss of mass of 0 031 units.

Aston's results show that each place in the periodic system may contain either a " simple " element or two or more isotopes, forming together (*e.g.*, Cl = 35 and Cl = 37) what was formerly regarded as a single element (*e.g.* Cl = 35·5). These isotopes have identical *chemical* properties and when the common element (*e.g.*, chlorine) consists of a mixture of isotopes it is nearly always the same mixture, since the atomic weight is invariable. In some cases (*e.g.*, boron) a slight variation in atomic weight has been described, and the isotopes of lead derived from radioactive changes (p. 94) have different atomic weights.

A more recent method for the detection of isotopes is the use of band spectra (p 225). The separation of the lines in a band depends on the mass of the molecule, and in some cases it is found that instead of a regular separation which would be expected from one kind of molecule only, there are really two (or more) sets of lines in the bands, due to isotopic molecules. The spectrum of hydrogen chloride, for example, shows lines corresponding to HCl^{35} and HCl^{37}. In this way the existence of oxygen isotopes of masses 16, 17 and 18 has been detected in the atmosphere, and also isotopes of carbon and nitrogen These were not revealed in Aston's experiments. There appear to be no theoretical restrictions on the occurrence of isotopes of elements.

The molecule $O^{16}O^{17}$ is present in atmospheric oxygen to the extent of 1 part in 5000 as a maximum. The $O^{18}O^{16}$ molecules are present to the extent of 1 part in 625. The existence of oxygen of mass 17 had

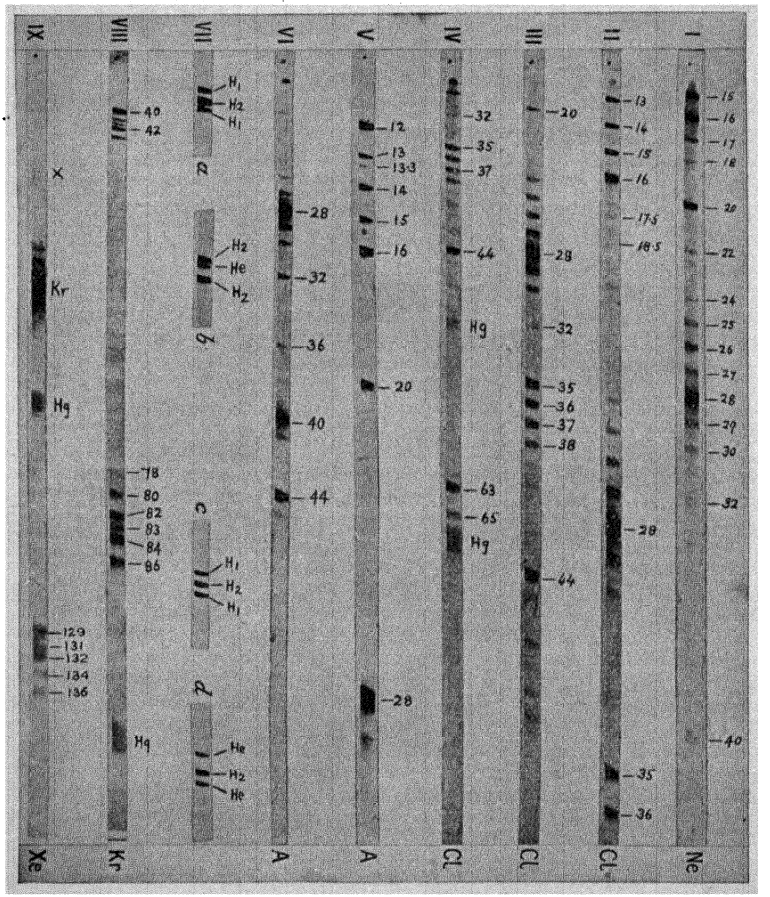


FIG. 212.—Mass spectra (Aston, 1921).

previously been reported by Blackett, by Kirsch and Pettersson, and by Harkins and Shadduck, from data obtained on collisions between α-particles and nitrogen nuclei (p. 454). One or two collisions per 100,000 result in combination of the α-particle (4) with nitrogen (14), forming an unstable isotope of fluorine which immediately ejects a proton (1) and becomes oxygen (17).

X-rays.—When the cathode rays strike a material target, which in the X-ray tube consists of a metal plate called an *anti-cathode*, 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 (Rontgen, 1895) have 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 it, charged particles 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 consist of **electromagnetic waves** similar to light but of much smaller wave-length (p. 738). The latter depends partly on the composition of the anti-cathode, or " target," and partly on the applied voltage.

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 and W. L. Bragg indicated that they suffer reflexion from crystal surfaces at definite angles of incidence in the same way as light from a diffraction grating.

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 identified d with the distance between planes in the crystal corresponding with the densest arrangement of the atoms. X-ray spectra thus provide the means of exploring the atomic architecture of crystals

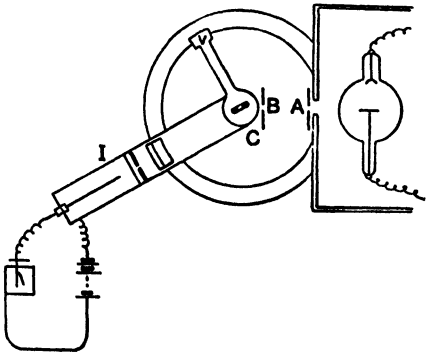


FIG 213.—X-ray spectrometer.

The original apparatus used by the Braggs is shown in Fig. 213. The rays from the anti-cathode 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 orders 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 example, 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.

By making use of the principle that the intensity of the radiation scattered from an atom is proportional to the number of electrons

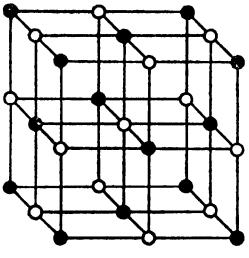


FIG. 214 —Arrangement of atoms in potassium chloride lattice.

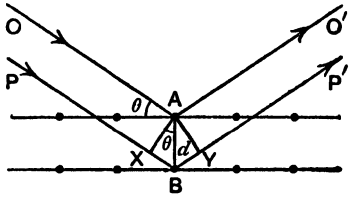


FIG 215 —Reflexion of X-rays from a crystal.

in the atom, and thus according to the modern theory of atomic structure (p. 452), to the atomic number 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. In this way the structure of such crystals was made out to be that shown in Fig. 214, the potassium atoms being represented by circles and the chlorine atoms by dots. The constituent particles of crystals of the salt are not, therefore, the chemical molecules KCl, but the atoms (or ions) K and Cl arranged in a cubic lattice.

Let OA, $O'A$ in Fig. 215 be the incident and reflected rays for the lattice point A, and similarly PB, $P'B$ for the lattice point B in a layer of atoms below that containing A. The difference in path for the two rays is $XB + BY = 2AB \sin XAB = 2d \sin \theta$, as is seen from the figure. The two rays are in phase and reinforce each other when this is a whole multiple, n, of the wave-length λ; $2d \sin \theta = n\lambda$. If d is known, λ can be found, and conversely if λ is known, d can be found.

For the value of d, the lattice constant of rock-salt is taken as standard. If in Fig. 214 we consider the atoms O as sodium and • as chlorine, and the side of the cube as a, then $d = a/2$.

There are 14 chlorine atoms, eight of which, at the corners, belong each to eight cubical lattices which may be packed around it, only one of these being shown The other six are on the faces, and each is common to two cubical lattices, one of which is shown. Hence, of the 14 atoms, a single cubical lattice has a share of eight 1/8 atoms, and six $\frac{1}{2}$ atoms, or $1+3=4$ atoms in all. Of the 13 sodium atoms shown, one is at the centre and 12 are at positions where each is shared by four lattices (one only shown), *i e*, in one lattice there are $1+3=4$ atoms The volume of the lattice is $a^3=8d^3$, where a is the side of the lattice and $d(=\frac{1}{2}a)$ is the distance between the planes of atoms. Thus d^3 is associated with the mass of one-eighth of 4 sodium atoms and 4 chlorine atoms, or half a molecule of NaCl This is $\frac{1}{2}\times 58\cdot0\times 1\cdot66\times 10^{-24}$ gm., where 58·0 is the molecular weight of NaCl (H = 1) and $1\cdot66\times 10^{-24}$ is the mass of the hydrogen atom But this mass is also equal to d^3 multiplied by the density of rock-salt, 2·17, hence $\frac{1}{2}\times 58\times 1\cdot66\times 10^{-24}=2\cdot17\times d^3$, or $d=2\cdot8\times 10^{-8}$ cm

By means of this value, the wave-length of any kind of homogeneous X-rays may be found by using rock-salt as the reflecting crystal and using the equation $2d\sin\theta=n\lambda$

The original method of Laue, viz., the production of a diffraction pattern of spots by a beam of rays passing *through* a plate of crystal cut in a particular direction, is also used in crystal analysis.

A third method of X-ray crystal analysis was developed independently by Debye and Scherrer and by Hull, and is called the powder method It has been shown above that a beam of X-rays is intensely reflected from the structural layers in a crystal only when it meets them at proper angles A powder will consist of innumerable small crystals orientated in a chaotic fashion, but there will always be a number of these which happen to be in correct orientation for the reflection of a beam of homogeneous X-rays transmitted through the powder. The latter is contained in a very thin glass tube placed parallel to the slit or in the direction of a beam transmitted through a small hole, or else the powder is spread out over a plate arranged for reflexion as in Bragg's apparatus. When the transmission method is used the pencil of rays is spread into a series of cones, the intersections of which on the photographic film produce a series of segments of circles arranged on each side of the central spot corresponding with the axial undeviated pencil (Fig. 216).

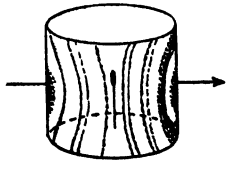


FIG 216.—The powder method of X-ray analysis

The cubic lattice.—Before the introduction of X-ray analysis, crystallographers had arrived at the conviction that in a crystal the constituent particles are arranged at the points of different types of **lattice** structures (p. 398), and even that the particles occupying the lattice points are often atoms, not molecules. The analysis of crystals by X-rays has completely confirmed this representation

The simplest lattice is the cubic, of which there are three types, viz., the **simple cubic lattice**, the **body-centred cubic lattice**, and the **face-centred cubic lattice**, shown as the last unit in Fig 234, and as *A* and as one of the eight units in *B* in Fig. 217 respectively. In the first the unit cell has eight atoms at its corners ; in the second there is in addition

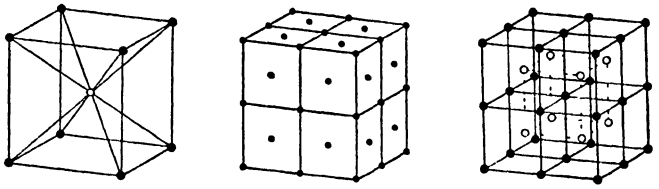


FIG 217 —Body-centred and face-centred cubic lattices

one atom at the centre of the cube, and in the third there are six atoms at the centres of the faces of the simple cubic lattice. The body-centred lattice may be produced by the interpenetration of two simple cubic lattices in such a way that the corners of one lattice occupy the centres of the cubes of the second as shown in *C*, Fig 217 In each unit cell of the body-centred type of lattice there are $1+8/8=2$ atoms, whilst the unit cell of the simple cubic lattice contains $8/8=1$ atom. The face-centred lattice can be formed from three simple cubic lattices arranged so that the centres of the faces in each unit cube are occupied : this unit cell then contains $8/8+6/2=4$ atoms.

The arrangement of the atoms in the face-centred cubic lattice is the *closest packing of spheres*. In a layer of equal spheres in contact there will be triangular spaces between every three, and in each triangular space another sphere may be placed to form a second layer. In Fig. 218 *a*, the centres of the lower spheres are shown as • and those in the second row as ○. A third layer may now be put on in two ways. Either they may be placed so as to move forward into the positions shown by ⊗, when the face-centred cubic lattice is obtained, built up on the octahedral surface (Fig. 218 *b*), or they may be arranged in the positions shown by •, *i.e.*, vertically above the atoms in the first layer, when a lattice with hexagonal symmetry is obtained, viz., the *hexagonal closest packing of spheres* : it consists of two interpenetrating hexagonal

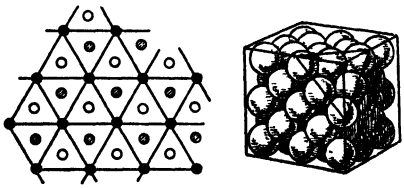


FIG. 218 —Close packing of spheres to form face-centred cubic and closest-packed hexagonal lattices

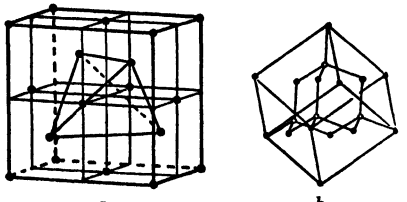
lattices, the first comprising the atoms in the layers 1, 3, 5, . , and the second the atoms in the layers 2, 4, 6, ... The ratio of the axes (p. 396) is $c : a = 1{\cdot}633 : 1$ for equal spheres.

The alkali halides belong to two types of lattice; probably each can exist in either form according to the conditions of temperature and pressure, and this is known to be the case for ammonium halides, two forms of which exist (1) The compounds CsCl, NH_4Cl and NH_4Br crystallise in the body-centred cubic lattice Each Cs atom is surrounded by 8 Cl atoms, but since each of the latter is shared by 8 unit cubes, the unit cell contains 1 Cs atom + 8/8 or 1 Cl atom, or one CsCl molecule Many metals (Li, Na, K, Cr, Fe, Mo, Ta, W) crystallise in body-centred cubic lattices, the atoms occupying the positions occupied by Cs and Cl atoms in CsCl. (2) The lattice of potassium, sodium and rubidium halides, and of ammonium iodide is the simple cubic (Fig. 214), with atoms of alkali metal and halogen alternately occupying the lattice points, and has been described above Each small cube contains $4 \times \frac{1}{8} = \frac{1}{2}$ an atom of each element Each halogen atom is surrounded by six equidistant metal atoms, and *vice versa*: the "molecule," *e.g.*, NaCl, seems to have disappeared. The metal and halogen atoms are really the ions, *e.g.*, Na^+ and Cl^-. The rock-salt lattice may be produced by the interpenetration of two face-centred cubic lattices, one of metal ions and one of halogen ions. Each crystallographic elementary cube (the whole figure) contains eight cubelets, and hence 4 atoms each of metal ion and halogen ion.

The following metals crystallise in *face-centred* cubic lattices: Al, Ca, Fe-γ, Co-β, Ni-α, Cu, Rh, Pd, Ag, Ce-β, Ir, Pt, Au, Pb, Th, Sr; the non-metal argon also crystallises in this system. In *body-centred* cubic lattices crystallise: Li, Na, K, V, Cr, Mn-α, Fe-α, Rb, Mo, Cs, Ta, W. (The different allotropic forms are designated α, β, etc.)

In *hexagonal* lattices crystallise Be, Mg, Ti, Co-α, Zn, Zr, Ru, Cd, Ce-α, Hf, and Os. The distances between the atoms in all these lattices are known, and vary from about 2·5 to 4·5 A.U

Metals crystallising in tetragonal lattices are indium and white tin; in the trigonal lattice (which may be regarded as an elongated cube) crystallise arsenic, antimony and bismuth.



a *b*

FIG. 219.—The diamond lattice.

The diamond lattice may be constructed by taking a face-centred cubic lattice of carbon atoms and putting a carbon atom in the centre of *alternate* cubelets as shown in Fig. 219 (*a*). Each carbon atom forms the centre of a regular tetrahedron, the corners of which are occupied by four

carbon atoms, as may be seen by drawing the lattice as in Fig. 219 (*b*). Diamond is an example of an **atomic lattice**, in which the atoms are linked by directed valency forces, as contrasted with the **ionic lattice** of an alkali halide, in which the separate charged ions are not linked by directed valencies but exert undirected electrostatic forces on one another. Silicon, germanium and grey tin crystallise in diamond lattices.

The graphite lattice consists of flat hexagonal rings of carbon atoms arranged in equidistant layers, such that the atoms in alternate layers are in similar positions in the hexagons (Fig. 295). In these planes, which correspond with the cleavage planes, each carbon atom is surrounded by *three* other equidistant atoms; the fourth valency is directed towards an atom alternately above and below the plane and at a much greater distance, and is hence very much weaker, as appears in the ready cleavage of graphite in the direction of the planes of hexagons.

The zinc blende lattice is similar to that of diamond : each zinc atom is at the centre of a tetrahedron of sulphur atoms and each sulphur atom at the centre of a tetrahedron of zinc atoms. The lattice of wurtzite, the second form of zinc sulphide, is formed from the zinc blende lattice by rotating alternate planes about an angle of 60° around the vertical axis. The tetrahedral symmetry is not disturbed but the arrangement (Fig. 220) is different from that in diamond.

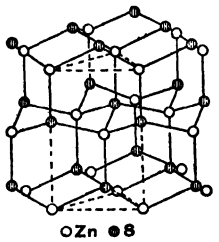


FIG 220 —Wurtzite lattice

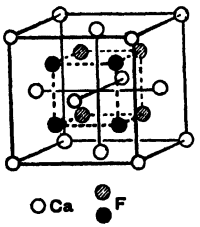


FIG. 221.—Fluorspar lattice

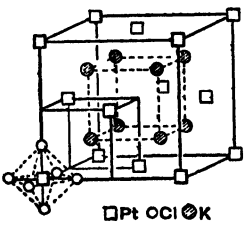


FIG 222 —Lattice of K_2PtCl_6

The fluorspar lattice is made up of a face-centred lattice of calcium ions penetrated by a simple cubic lattice of fluorine ions, so that the corners of this lie on the quarter lengths of the diagonals joining the calcium ions (Fig. 221). Each Ca^{++} ion is surrounded by $8F^-$ ions, each F^- ion by 4 Ca^{++} ions. In the elementary cube are $8/8 + 6/2 = 4$ Ca^{++} ions and $8F^-$ ions (corresponding with the formula CaF_2). The F^- ions lie on the corners of a half-sized inner cube, as shown.

An interesting cubic lattice is that of such co-ordination compounds (see p. 461) as K_2PtCl_6 (Fig. 222). This may be regarded as a fluorspar lattice in which F^- is replaced by K^+, and each Ca^{++} by

$PtCl_6^{--}$. In the complex ion $PtCl_6^{--}$, each central Pt atom is surrounded by six Cl^- ions in octahedral arrangement, thus confirming the assumption of Werner. (For simplicity only one $PtCl_6^{--}$ is shown in full.)

Finally, as an example of a more complicated lattice we may consider calcite (Fig. 223). This may be regarded (not quite strictly) as a deformed rock-salt lattice. If the latter is imagined stood on a diagonal (looked at from above in the figure), all the Na^+ ions replaced by Ca^{++} ions and all Cl^- ions by carbon atoms, each of the latter surrounded by a triangle of 3 oxygen atoms in a plane at right angles to the diagonal (the plane of the paper), then on account of the space occupied by these oxygens the cube expands in a horizontal direction and gives the cleavage rhombohedron of calcspar. Calcium and carbon atoms are spaced at equal intervals along the axis of the crystal, and each carbon is surrounded by three oxygens, forming the carbonate ion CO_3^{--}.

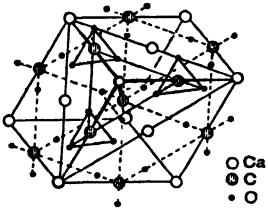


FIG. 223.—Calcite lattice

The existence of separate ions in crystals such as rock-salt has been made probable by (1) the intensities of X-ray reflections from such crystals (Debye and Scherrer, Li^+ and F^- in LiF; Gerlach and Pauli, Mg^{++} and O^{--} in MgO); (2) the reflexion of infra-red rays from crystals (*residual rays*); (3) the ionisation of such crystals in solution and in the fused state.

Vegard (1917) showed that *mixed crystals* of NaCl and KCl gave a single X-ray powder diagram very similar to that of both components, and not a superposition of the diagrams of the two kinds of crystals Hence in this case and others investigated the solid is homogeneous and is not formed, for example, by the superposition of very thin layers of the separate crystals In the ideal case the constituent atoms (or molecules) of a mixed crystal are uniformly distributed. In the case of alloys this uniform state is only reached after long standing, annealing, etc., when the atoms change their places in the crystal.

Experiment indicates that actual crystals are not perfect lattices but consist of aggregates of innumerable small " blocks," each part of a perfect lattice, joined together by loose ions which alone take part in the conduction of heat and electricity. Between these aggregates are, therefore, " cracks," similar to the layers of mortar between the bricks in a house, and the irregularly arranged ions in the cracks are those which cement the blocks together and act as conductors (Smekal, 1927). Each lattice block may contain about 10,000 ions or molecules

Atomic numbers.—Barkla, and Kaye (1909), found that a solid element when bombarded by a sufficiently rapid stream of cathode rays, emits a characteristic *X*-radiation. This may be resolved into a

spectrum by reflexion from a crystal, as explained on p. 427. Moseley (1913–14) 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. Several kinds of rays, the *K*, *L*, *M*, *N* and *O*, have been detected, the first two by Moseley and the others by later workers The *K*-radiations are of the shortest wave-length, and are emitted by elements of small atomic weight to those of highest The *L*-radiation of elements, shown from copper and elements of higher atomic weight, is of longer wave-length than the *K*-radiation, and the *M*, *N*, and *O*-radiations, shown by heavier elements, are of still longer wave-length The *K*-radiation of each element consists of four lines, but these appear as two pairs in each of which the two lines are very close together and were not resolved in Moseley's photographs The *L*-radiation gives a larger number of lines than the *K*, in the case of tungsten, Siegbahn measured eighteen lines in the *L* spectrum

The *K* spectra obtained by Moseley consisted in all cases of two lines (really the two *K* pairs), one stronger than the other, the wave-lengths of which decreased in a regular manner as the atomic weights of the elements increased. The square-roots of the frequencies of corresponding strong K_α lines in the spectra of successive elements taken in the order of their positions in the Periodic Table, when plotted against the ordinal number of the element in this table (atomic number, p. 412), gave practically a straight line. In Fig. 224, the square roots of the frequencies of the *K*, *L*, *M*, and *N* series are plotted against the atomic numbers of the elements. If ν is the frequency of the K_α line; ν_0 is a constant (Rydberg's constant); and N is the atomic number, then Moseley found that:

$$Q = \sqrt{\nu/\tfrac{3}{4}\nu_0} = N - 1.$$

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; Te, I) 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. The total possible number of elements from hydrogen to uranium is thus found to be 93. Moseley's method provides a means of definitely finding the places in the sequence of atomic numbers

where there are missing elements. In this way, elements number 43, 61, 72, 75, 85 and 87 were found to be missing. The first five were

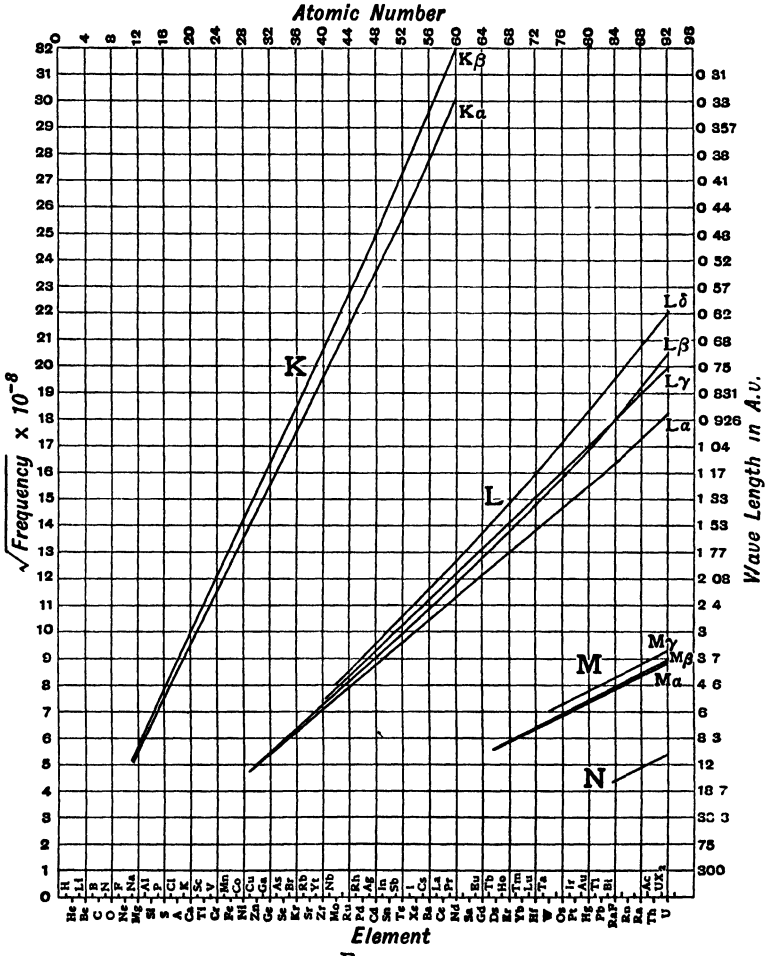


FIG 224

discovered by X-ray spectroscopy as masurium, illinium, hafnium and rhenium, respectively, and eka-iodine (85) and eka-caesium (87) have also been reported.

Since all the isotopes of an element occupy the same place in the Periodic Table they have the same atomic number and the same X-ray

spectrum. This has been confirmed, for example, with some of the isotopes of lead.

Moseley's results indicate that the atomic number of an element is a property of the atom of a more fundamental character than the atomic weight, and he suggested that this was the net positive charge on the central nucleus of the atom.

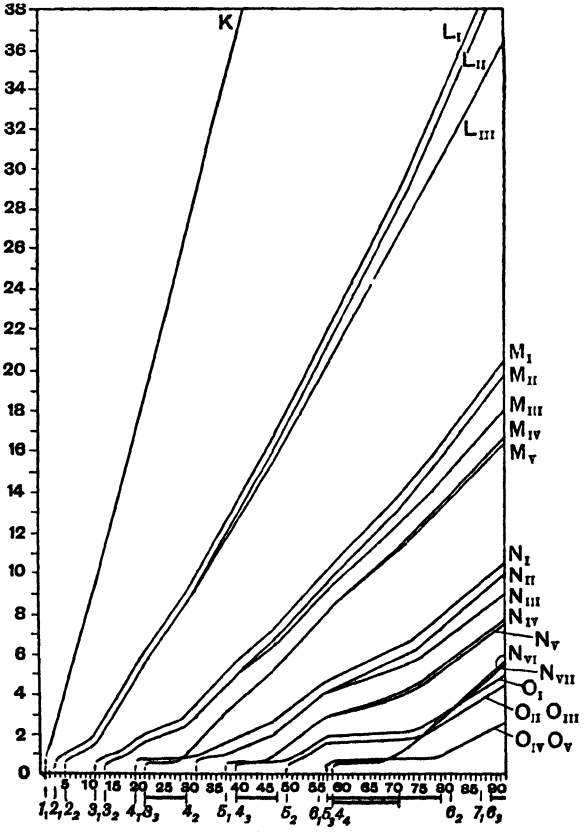


FIG 225.

Refinements in X-ray spectroscopy have shown that the linear character of the *L*, *M*, *N* and *O* series is only approximate, and that the curves show definite changes of direction (Fig. 225). The ordinates are here, not $\sqrt{\nu}$, but the values of $\sqrt{\nu/\nu_0}$, where ν_0 is Rydberg's constant. These breaks are very important in the theory of atomic structure, since they appear at the beginning and end of successions of

elements which are closely related in chemical properties, *e.g.*, Sc to Cu; *Y* to Ag; etc. In these the transition from one element to the next, instead of leading to a marked change of properties as usual, produces little change and since the relation to the transitional elements of Group VIII is apparent, these sequences of elements are called "transitional series." This preservation of essential chemical properties is most apparent in the group of the rare earth elements (Nos. 57–71). An explanation of this behaviour on the basis of the theory of atomic structure is given on p. 469

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 blende (zinc sulphide).

(3) The ionisation of gases 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. 226). 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 eye-piece, 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 analytical instrument known, since 10^{-12} gm. of material can readily be recognised.

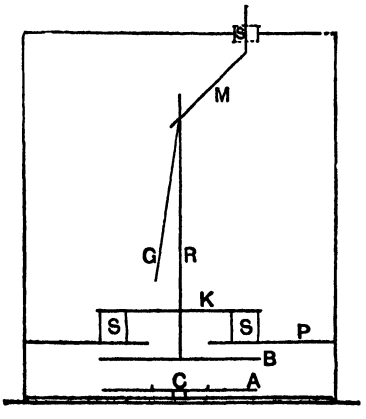


FIG. 226.—Gold-leaf electroscope.

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 due to the presence in the ore of a new element 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 doubled.

The separation of the radium from pitchblende is a laborious process. The radium accumulates in the barium separated from the residues Radium and barium chlorides are separated by a long series of fractional crystallisations, with the bromides eight crystallisations suffice

A former source of radium compounds was the *carnotite of* Colorado, with 5 to 10 mgm. of Ra per ton Rich deposits of pitchblende in the Belgian Congo superseded the carnotite, and there are rich deposits of pitchblende in the Great Bear Lake territory in N W. Canada

Radium chloride melts at a high temperature and solidifies to a glassy mass which, unlike the salt containing water, emits an intense bluish-violet light.

Radium compounds are isomorphous with those of barium; the ratio of chlorine to radium in the chloride is 35·5 : 113, so that on the assumption that the formula is $RaCl_2$, the atomic weight of radium is 226 Honigschmid from the ratio $RaCl_2 \cdot RaBr_2$ found Ra = 225·97 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 forms hydrogen peroxide and 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. Glass is coloured violet or brown by radium rays. The colour is discharged by heating nearly to the softening point.

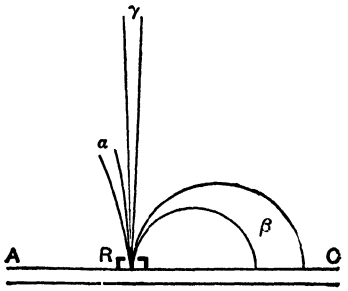


FIG 227.—Magnetic deflection of rays from radium

Metallic radium was obtained by Mme. Curie and A. Debierne 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. 960°, which rapidly tarnishes in the air, forming a nitride, 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, it was found that radium emits **three kinds of rays** (Fig. 227):

1 The **α-rays**: positively charged particles, easily absorbed by thin metal foil, and having a limited range in air (7 cm when emitted from RaC′).

2 The **β-rays**: negatively charged particles, identical with free negative electrons, emitted with speeds approaching the velocity of light, and often capable of penetrating thin sheets of aluminium.

3 The **γ-rays**: not deflected by magnetic fields, consisting of waves identical with very short X-rays (wave-length, $1{\cdot}3 \times 10^{-7}$ to 7×10^{-10} mm.), and capable of penetrating several cm of lead.

The deflections produced by a magnetic field are seen in Fig 227 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.

The α-rays.—The phosphorescent effects of radium are mainly due to the α-rays, which on account of their relatively large mass and high velocity ($\frac{1}{15}$ to $\frac{1}{10}$ that of light), possess considerable kinetic energy. In the spinthariscope (p. 225) 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 Lord Rutherford, who found for them the value e/m (charge/mass) $= 5{\cdot}07 \times 10^4$ cmb./gm , and Rutherford and Robinson $4{\cdot}82 \times 10^4$ cmb./gm., almost exactly half that for the hydrogen ion in electrolysis. They may, therefore, consist of atoms of weight 2 with one unit positive charge, or atoms of weight 4, *i.e.*, helium, with two unit charges. By sealing radium emanation in a thin glass tube, Rutherford and Royds (1908) 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. 228). Rutherford and Geiger determined the charge directly by measuring the charge conveyed by a counted number of α-particles, and found it to be $3{\cdot}1 \times 10^{-19}$ cmb., hence $m = 0{\cdot}66 \times 10^{-23}$ gm. But the mass of the hydrogen atom is $1{\cdot}6 \times 10^{-24}$ gm., hence the atomic weight of the α-particle is very approximately 4. The α-particle was

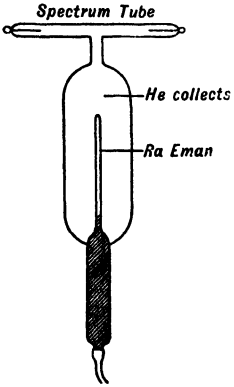


FIG. 228.—Production of helium from radium emanation.

thus independently found to consist of a particle of mass 4, with two unit positive charges, a helium atom which has lost two negative electrons. The diameter of the α-particle is very small (*c.* 10^{-13} cm) compared with that of the helium atom (*c.* 10^{-8} cm.). The speed with which α-particles are emitted by radium is about 2×10^9 cm. per sec., hence the corresponding kinetic energy is $1{\cdot}34 \times 10^{-5}$ erg, or $2{\cdot}2 \times 10^9$ times that of a gas molecule at 0° (p. 221). It is this large energy which accounts for the phosphorescence effects, and for most of the heat evolved by radium, which amounts to over 128 g. cal. per gm. of radium and its equilibrium products per hour. Each α-particle detaches one electron from each molecule of gas it ionises, and the α-particle from RaC′ ionises 237,000 molecules in its passage through air.

The β-rays.—Although the β-rays are more penetrating to matter in bulk than the α-rays, on account of their smaller size and higher velocity, yet they are more deflected in their encounters with individual atoms than are α-rays. Their paths, therefore, deviate very much from straight lines, as has been shown by the Wilson method (p. 446); they are frequently deflected through 180°. On account of its smaller mass and kinetic energy, a β-particle produces much less ionisation for 1 cm. path than an α-particle: the ionisation produced consists in the detachment of one electron from each molecule of gas, leaving a positive ion. The total number of ions produced in air by β-rays from 1 gm. of radium in equilibrium with its products of disintegration is 9×10^{14} per sec.

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 condensed in a tube cooled in liquid air. By the direct weighing of an exceedingly small volume of this gas, called radium emanation, on the micro-balance its atomic or molecular weight (on the assumption that it is monatomic) was found to be 222·4. 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 (Latin *nitidus* = shining), but **radon** is now used. It has a characteristic spectrum, similar to that of xenon, and is distinctly soluble in water.

The unit of radioactivity is the *curie*, which is the activity of 1 gm. of radium, equivalent to about 0·6 cu. mm. of emanation.

Ramsay and Soddy observed that the emanation of radium, or radon, on standing gradually lost its characteristic spectrum, whilst the helium spectrum appeared. The conversion of radon into helium was definitely proved by the experiment of Rutherford and Royds

already mentioned. $3{\cdot}7 \times 10^{10}$ atoms of helium are produced from 1 gm. of radium per second. The emanation is continually undergoing transformation into helium and other products, and fresh emanation is constantly produced from the radium. **Radioactive equilibrium**, in which a parent element is producing a decay product at the same rate as the latter is undergoing further change, although it is a stationary state, is not the same thing as ordinary chemical equilibrium, since the changes are not reversible. 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.

The atomic weight of radium is 225·97; the observed density of radon is 111·2, hence the atomic weight is 222·4. The difference is 3·6, 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 (226) = α-particle (4) + Rn (222). Two gases, helium and radon are thus the first product from the solid radium.

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. Experiments show, however, that radium is constantly changing into helium and radon. Each of these is an element in the same sense as radium. Radon, 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 either of α-rays, or of 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 five β-particles are emitted. The atomic weight of radium is 226, and the five α-particles have a mass of $5 \times 4 = 20$, hence the atomic weight of the final product will be $226 - 20 = 206$. The atomic weight of lead is 207·2, hence it would seem probable that the final product of the disintegration of radium is an isotope of lead. This has been confirmed.

In the description of the properties of radium, it has been assumed that its atoms and those 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 explains all the observed phenomena.

Average life and half life.—An atom of a radioactive element is at any moment liable to explode. The expectation of life 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 radio-element is characterised by its average life, which may vary from some millionths of a second to millions of years, according to the stability of the element. In radioactive equilibrium the amounts of parent substance and disintegration products are proportional to their half-life periods.

Radioactivity of uranium.—In 1900 Crookes found that if an ordinary uranium salt 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 contains a substance called **uranium-X_1**; on standing it became inactive, whilst the solution regained its activity and yielded another specimen of uranium-X_1. Uranium is therefore capable of growing uranium-X_1.

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, called **uranium-I** and **uranium-II.** U II passes directly into ionium by emission of an α-particle, whilst U I passes into UX_1. From UX_1 two products are obtained, each by emission of a β-particle, viz, UX_2 (99·7 per cent.) and UZ (0·3 per cent), each of which, by emitting a β-particle, passes into U II. This is an example of a **branch chain** in disintegration. The complete series of transformations of uranium, which includes that of radium, of which uranium is the parent, is given in the table on p. 444. The table also gives the transformations in the actinium series and in the independent thorium series.

Radioactivity of thorium.—In 1902 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 precipi-

tate 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. It is now known that Th-X is formed from Th through three intermediate products, called **mesothorium-I, mesothorium-II,** and **radiothorium.** When Th-C is reached, the atoms may disintegrate further in two different ways. Thirty-five per cent. of the Th-C atoms emit an α-ray forming Th-C″, which then emits a β-ray, forming lead; whilst 65 per cent. of the Th-C atoms emit β-rays, forming Th-C′, which then emits an α-particle, forming lead. No detectable rays are emitted by Ms-Th_1, so that the production of Ms-Th_2 from it is called a **rayless change.** Probably feeble β-rays are emitted.

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 immediate parent of the actinium series is a variety of uranium called uranium-Y This emits a β-ray, forming an element discovered by Soddy in 1917, called by him **eka-tantalum,** and by Hahn (an independent discoverer), **protoactinium,** which gives rise to actinium by emission of an α-particle Protoactinium, although an element of Group V, is chemically similar to thorium and zirconium rather than tantalum, and accumulates in the zirconium phosphate in the residues from the refining of radium from pitchblende Protoactinium pentoxide is a heavy white powder with feebly basic properties. The final product of the actinium series is an isotope of lead

The position of radio-elements in the periodic system.—The position of an element in the periodic system is fixed by its atomic number, which is equal to the positive charge on the nucleus of the atom, measured in terms of the electronic charge as unit. The atomic numbers of uranium, thorium and radium are known from the positions of these elements in the Periodic Table (p. 411), and the atomic numbers of all disintegration products may be calculated by subtracting 2 for each α-particle emitted (loss of charge $+2$), or adding 1 for each β-particle emitted (loss of charge -1). The positions of the radioactive disintegration products in the Periodic Table are thus seen to be governed by a simple rule. This states (Russell, Fajans, and Soddy, 1913) that in an α-ray change, viz, a 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 radon, an inactive gas of the zero group; the expulsion of a β-particle from RaD,

an element of Group IV, leads to the formation of RaE, an element of Group V.

The series of radio-elements and their transformations are shown in Table II, in which their positions in the periodic table are evident. More than one kind of atom may occupy the same place in the system, specified by the atomic number given at the foot of the table. The different kinds of atoms occupying the same position in the table are isotopes (see p. 94); they are inseparable one from another by chemical processes and behave chemically as identical elements. The radioactive isotopes may be distinguished, however, by their rates of disintegration, and by the nature of the elements from which they are derived or of the products to which they give rise. Isotopes are also differentiable by their atomic weights and by their densities, since their atomic volumes are identical.

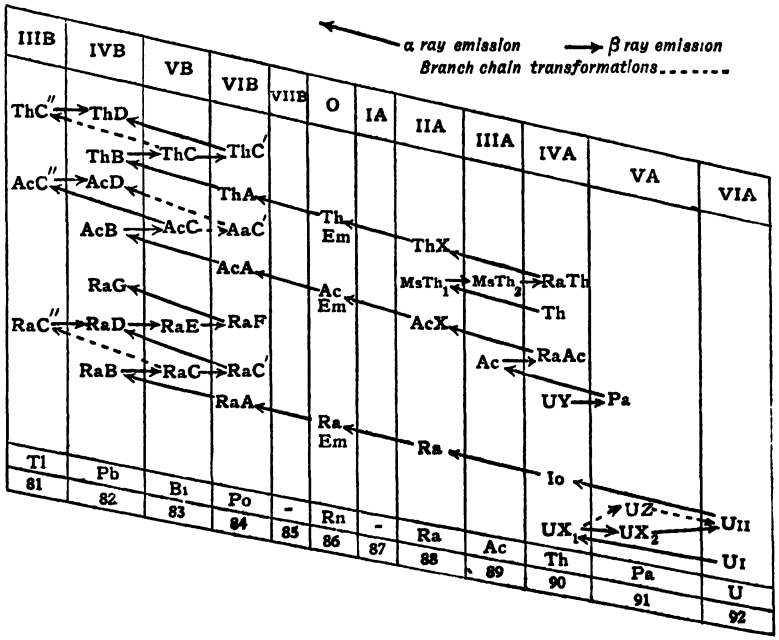


TABLE II.—Radioactive Series.

The molecular solubilities of compounds of isotopes are identical: those 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 X-ray spectra of ordinary lead and of uranio-lead were found to be identical within the error of 0·0001 A.U. (see p. 434). The arc spectra differ by about 0·005 A.U., which is a measurable amount (Merton, 1919). It is also possible that isotopes may have different vapour pressures.

Table II shows that the three main radioactive series extend over ten places in the periodic table, the places occupied by the halogens and the alkali-metals, viz., Groups I and VII, being skipped, although potassium and rubidium in Group I show feeble β-ray activity. Samarium in Group III shows feeble α-ray activity.

In the ten occupied places in the last two periods there are over forty distinct types of atoms, characterised by specific radioactive properties and atomic weights, but these represent only ten chemically different elements. The chemical and spectroscopic characters of eight of these, viz., Tl, Pb, Bi, Rn, Ra, Th, Pa, and U, have been firmly established, and the places occupied by them accommodate nearly all the known radio-elements.

The tendency of workers on radioactivity was to regard isotopes as different elements; since, however, they are identical in chemical properties it was suggested by Paneth (1916) that they should be regarded as varieties of elements, the latter being substances which cannot be simplified by ordinary physical or chemical means. Perhaps the most satisfactory definition, closely related to Moseley's law (p 434) is that an element is defined by its atomic number.

Deflection of α-rays in gases.—The α-particles, charged helium nuclei emitted by a radioactive substance, on passing through air produce gaseous ions which can act as centres 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 condensed on the ions, which can be photographed. In this way C. T. R. Wilson obtained the photograph shown in Fig. 229. The paths of two single α-rays are shown in Fig. 230. 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 left-hand track shows a large deflection at its end, and a very small spur is seen going off in the other direction. The latter represents the track of the atom of gas which has stopped the α-particle; this has imparted to it a recoil velocity, and the angle between the track and the original direction of the α-particle gives the relative masses of the striking and struck particle, in agreement with the ordinary laws of elastic collision (oxygen $16{\cdot}72 \pm 0{\cdot}42$; helium 4·03). The method provides a means of determining the masses of single atoms (Blackett, 1922).

The structure of the atom.—The sudden and often large deflection of the α-particle at the end of its track, shown in Fig 230, 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

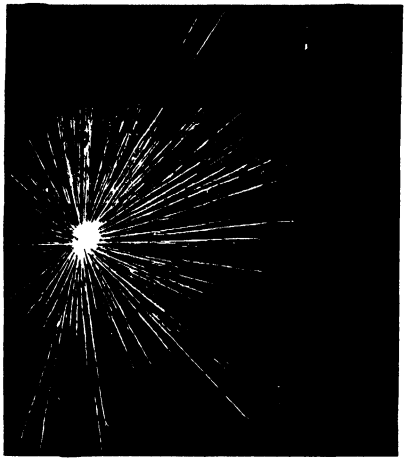


FIG 229.—Tracks of α-rays

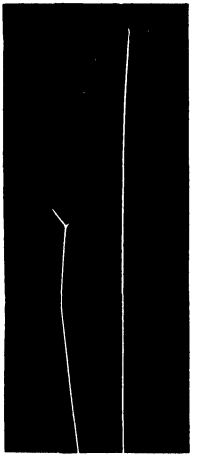


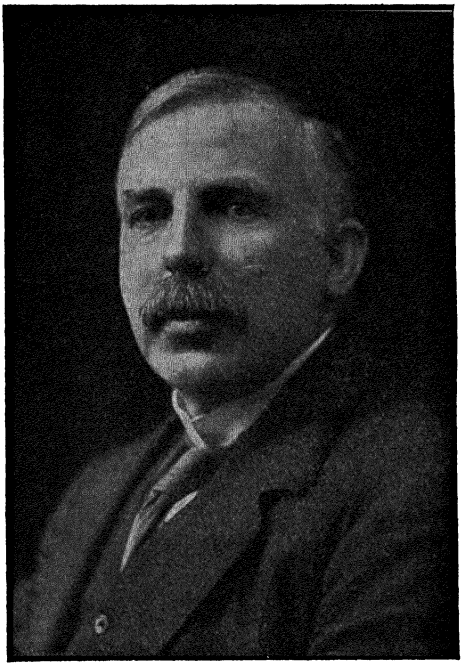
FIG 230.—Tracks of two α-rays (enlarged).

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 from the deflections by the inverse square law shows that the two charges must have approached within a distance of 10^{-13} cm., much 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 it must contain negative electrons. The simplest assumption is that it consists of a small positive nucleus surrounded by electrons, possibly revolving in orbits about the nucleus, the diameter of the outer orbit being of the order of the diameter of the atom. The rest, the greater part of the atom, is empty space. The electrons have a very small mass, so that the mass of the atom must be concentrated in the positive nucleus. This theory of the structure of the atom is due to Rutherford (1911).

The hydrogen atom is assumed by Niels Bohr (1913) to consist of a nucleus of charge +1, in this case the proton (p 244), with one electron of charge −1 revolving around it in a circular orbit, the whole

being electrically neutral (Fig. 231). The nucleus of the helium atom (mass 4) contains four protons and two electrons ; it has a charge (and



[*Russell, London.*

LORD RUTHERFORD.

atomic number) of $4 - 2 = 2$, and is identical with the α-particle. In the helium atom there are two other electrons outside the nucleus.

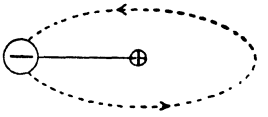


FIG. 231.—Structure of hydrogen atom (Bohr).

The series of atomic numbers suggests (van den Broek, 1913) that successive atoms counting from hydrogen have nuclei containing one additional positive charge for each step in atomic number. This has been confirmed experimentally by the deflection of α-rays by various atoms.

By measuring the scattering of α-particles passing through thin sheets of metal, Chadwick (1920) was able to calculate the charge on the nucleus of the metal atom, on the assumption that the deflections of the α-particles were caused by the approach of the positive helium nuclei towards the positive nuclei of the atoms. For platinum, silver, and copper the nuclear charges were found to be 77·4, 46·3, 29·3, *i.e.*, in

very good agreement with the atomic numbers, 78, 47 and 29, of these elements. Chadwick measured the fraction f of the total number of α-particles scattered through a given angle, ϕ, which is related to the charge on the nucleus (Z) by the formula .

$$f = KZ^2 \operatorname{cosec}^4 \tfrac{1}{2}\phi,$$

where K is a constant which can be calculated for a given metal foil, arrangement of apparatus, and speed of α-particle. The number of scattered α-particles is counted by the scintillation method (p 225).

In chemical changes only the outer electrons are disturbed. The ionisation of potassium, for example, implies a loss of one outer electron, the nucleus and the other electrons surrounding it remaining unchanged. The shift of outer electrons 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 (swift electrons) are emitted, that disruption of the nucleus occurs Except in the case of hydrogen, the nucleus contains negative electrons as well as positive protons. There must always be a net positive charge on the nucleus to maintain neutrality with the outer electrons The α-particle consists of four protons plus two nuclear electrons, since it has a net positive charge of two units. The helium atom has two outer electrons in addition.

The Bohr atom has given an explanation of the origin of spectra. Whilst the electron revolves in an orbit it emits no energy as radiation, but when it springs from one orbit to an orbit with less energy (nearer the nucleus) it emits energy according to the quantum law (p 199) The frequency of the line emitted is given by the quantum relation $\nu = \Delta E/h$, where ΔE is the energy difference between the two electronic orbits concerned

In the atom we recognise two distinct regions—the nucleus and the outer electrons. The nucleus is exceedingly small in comparison with the whole size of the atom, and *the net positive charge of the nucleus is equal to the atomic number of the element.* The outer negative electrons are sufficient in the case of the neutral atom to balance the positive charge of the nucleus, or n fewer or greater in the case of the n-valent positive or negative ion. The majority of these electrons are situated at relatively great distances from the nucleus : in the heavier atoms they are arranged in several shells, or orbits.

The transmutation of elements.—Although the rate of disintegration of the atoms of radioactive elements cannot be influenced by any known means, it has been found that the collision of swift α-particles or of protons with atoms of other elements can cause the disruption of the atomic nuclei, leading to the ejection of fragments of the atom with such velocities that their presence may be detected, for example, by the scintillation method (p. 225).

Rutherford in 1919 extended an observation by Marsden (1914), according to which the protons (H-nuclei) ejected by the α-particles of Ra-C by collision with hydrogen atoms had a range of about 28 cm. in air as determined by the scintillation method on a zinc sulphide screen, whilst the range of the α-particle is about 7 cm. The identity of the long range particles with H-nuclei was established by the measurement of e/m by deflection in electric and magnetic fields.

Rutherford, partly in collaboration with Chadwick, was able to show that long range H-particles are also produced by the bombardment of certain elements, such as boron, nitrogen, fluorine, sodium, aluminium and phosphorus, free from hydrogen, by α-rays, and thus to provide a direct proof that the nuclei of these atoms contain H-nuclei or protons, and at the same time the first definite case of the artificial disintegration of an element The actual number of atoms disintegrated is in any case exceedingly small.

Blackett (1922) was able by the Wilson method (p. 445) to obtain photographs of collisions involving the expulsion of protons from atoms. When α-particles (mass 4 , nuclear charge 2) bombard nitrogen atoms (mass 14 ; nuclear charge 7) they apparently enter the nucleus of the atom, producing a particle of mass $14+4=18$, and nuclear charge $7+2=9$, *i.e.*, an isotope of fluorine (see Table III). This nucleus then emits a proton (mass 1 , charge 1), leaving a nucleus of mass $18-1=17$, and charge $9-1=8$, *i.e.*, an isotope of oxygen (see Table III). The branch at the end of the α-ray track shows only two prongs, corresponding with the H-particle and the new nucleus. This is an example of the artificial building up of an element (oxygen) from a lighter element (nitrogen), and may be represented as follows, the lower figures giving the masses, and the upper the charges, of the nuclei :

$$N_{14}^{7}+He_{4}^{2}=O_{17}^{8}+H_{1}^{1}.$$

Very penetrating radiation emitted from beryllium bombarded with α-rays is supposed to consist of **neutrons**, very small particles of zero charge (atomic number 0) and mass 1. The other product is, hypothetically, an atom of carbon :

$$Be_{9}^{4}+He_{4}^{2}=C_{12}^{6}+H_{1}^{0}.$$

Protons of high velocity and energy are capable of disintegrating some elements of atomic masses $4n+3$, where n is a whole number, and it is suggested that the addition of a captured proton leads to the formation of an α-particle in the nucleus $(3+1=4)$, which may then be emitted, thus leading to artificial transmutation, in this case with the production of an element of smaller mass. Neutrons may produce similar effects

$$Li_{7}^{3}+H_{1}^{1}=He_{4}^{2}+He_{4}^{2}, \qquad N_{14}^{7}+H_{1}^{0}=B_{11}^{5}+He_{4}^{2},$$

$$F_{19}^{9}+H_{1}^{1}=He_{4}^{2}+O_{16}^{8}, \qquad O_{16}^{8}+H_{1}^{0}=C_{13}^{6}+He_{4}^{2}$$

Evidence has been obtained (1933) of the existence of the positive electron, or **positron**, with the same mass as the negative electron, or **negatron**, and of equal but opposite charge. These are produced by the action of the neutrons and γ-rays emitted from lead or aluminium by the action of the radiation from the action of polonium on beryllium, and also in the disintegration of atoms by cosmic rays Previously, the proton was the smallest known mass of positive charge The neutron may be regarded as a close association of a proton and a negatron, or as a fundamental particle, in which case the proton is a complex of a neutron and a positron.

It is possible that the theory of the structure of atomic nuclei at present generally accepted, may undergo some modification. Instead of the proton and electron being considered as the fundamental units of matter, these may be taken as the negatron and positron (particles of free negative and positive electricity of very small mass) and the neutron, or uncharged particle, with a mass sensibly equal to that of the hydrogen nucleus The latter, the old proton, would then be regarded as a combination of a neutron and a positron. The theory of valency, and most of the chemical applications of modern atomic theory, would not be much affected, as these are concerned mainly with electrons outside the atomic nucleus

The Lewis octet theory.—In building up more complex atoms, *e g*, lithium, the two outer electrons of the helium atom seem to be retained in an innermost shell next to the nucleus. The successive atoms from hydrogen to neon may be supposed to be constituted by addition of protons and electrons to the nuclei, the *mass* being the number of protons in the nucleus and the *atomic number* the net positive charge of the nucleus, *i.e.*, the number of protons less the number of electrons in the nucleus. An atom of atomic weight A and atomic number Z has a nucleus composed of A protons and A – Z electrons, surrounded by Z other electrons

When the outer shell of 2 electrons has been completed in the case of helium a new shell begins, containing from 1 electron in the case of lithium to 8 electrons in the case of neon. The structure of atoms of higher atomic number than neon is a continuation of this process, a new 8-electron shell being completed in the case of argon.

The outer *octet* of eight electrons in the stable inert gas structures of neon or argon naturally suggests an arrangement at the corners of a cube, with the nucleus and the inner shells (including the very stable pair of electrons added in the helium atom) inside it. This structure is postulated by G. N. Lewis. The outermost layer of electrons in an inert gas atom is supposed always to contain eight electrons. In Fig. 232 the nucleus with two outer electrons is supposed to be contained in all the cubes.

TABLE III. STRUCTURES OF ATOMS.

Element	Mass = No of protons in nucleus.	Atomic number = net + charge of nucleus	No of nuclear electrons	No of outer electrons
H	1	1	0	1
He	4	2	2	2
Li	7	3	4	1
Be	9	4	5	2
B	11	5	6	3
C	12	6	6	4
N	14	7	7	5
O	16	8	8	6
F	19	9	10	7
Ne	20	10	10	8

This theory gives a graphic picture of the manner in which atoms interact to form ions, *e.g.*, the Li atom with one outer electron reacts with the F atom with seven outer electrons to give the F′ ion

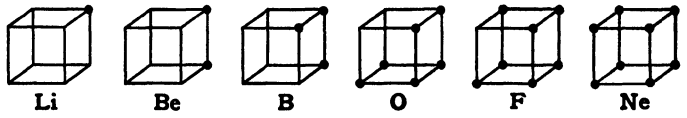


FIG 232.

(F atom + one electron) with one completed octet, and the Li ion with the two outer electrons of helium as external shell, the single outer *valency electron* being transferred to the fluorine.

In the case of the Cl atom, this will have an inner octet (the neon structure) and seven outer electrons. On reaction with Na, the Cl ion with the completed external octet of argon is formed by gain of one electron, leaving a complete octet of the Na ion.

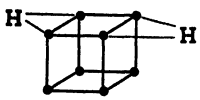


FIG 233

In the case of non-electrolytes, Lewis assumes that *a pair of electrons is shared* in common by two atoms to form a single valency bond. Thus, the water molecule is formed by the oxygen atom with six outer electrons, and two hydrogen atoms each with one outer electron, *sharing* two pairs of electrons so that the octet is completed around the oxygen (Fig. 233).

The formation of a molecule of chlorine from two chlorine atoms, each with 7 electrons is represented by:

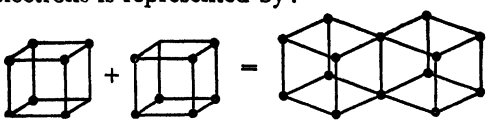


FIG. 234

An ordinary double bond is constituted by *four* shared electrons. Thus the formation of an oxygen molecule is represented by

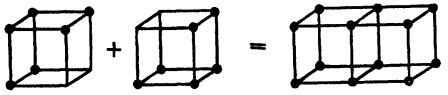


FIG 235

The formula for CO_2 is shown in Fig. 236, the central cube representing the carbon atom with four electrons; the four shared electrons constitute a double bond: O=C=O, and each atom is surrounded by eight electrons.

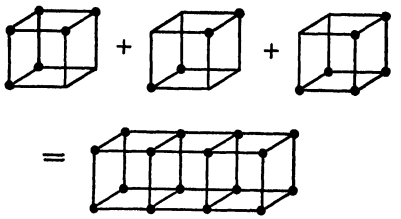
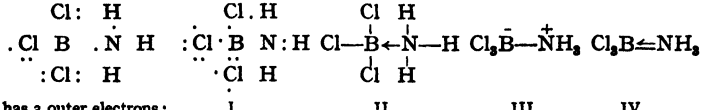


FIG 236

In writing formulae each electron is represented by a dot; two dots represent an ordinary valency bond (covalency). Electrons which belonged to different atoms may for clearness be distinguished by using crosses, etc., but in the resulting bond there is no difference between the electrons:

H—O—H	H—Cl	O = C = O
H × O × H	H × Cl :	O : × C × : O
H : O : H	H · Cl :	O : : C : : O

In some cases the pair of electrons may arise by *one* atom giving an isolated pair of electrons to the outer shell of another atom so as to complete an octet. Ammonia has a " lone pair " of electrons on the nitrogen and can " donate " these to the boron in boron trichloride, surrounded by six electrons, in order to complete the octet:

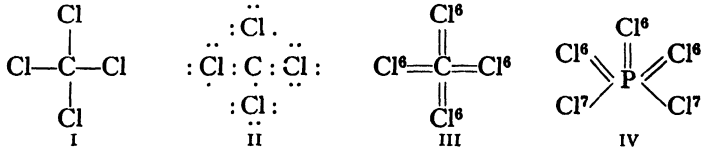


B has 3 outer electrons; N has 5; Cl has 7, H has 1

I II III IV

This may explain the formation of additive (molecular) compounds; the **co-ordinate link** so formed may be shown by drawing an arrow from the atom providing the pair of electrons as in II. Since this atom, by the shift of negative electrons away from it, has become more positive and the other atom more negative, this type of link may also be called a **semi-polar double bond** and represented as in III and IV, which express the idea that it consists of one polar bond (due to transfer of electrons) plus one covalent bond, due to the pair of shared electrons; when so regarded it counts as two valencies.

A single *shared* electron may also be represented by a line between the two atoms which share it, *unshared* electrons being represented by a superscript number:



I II III IV

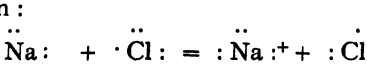
Formulae I and II show the usual graphic formula and the electronic formula, respectively, of CCl_4; formula III is written in the way just explained. Formula IV is a suggested formula for PCl_5. Since the valency electrons are accounted for, the symbols of the elements stand for the atomic **cores**, *i.e.*, nuclei plus completed shells of electrons other than valency electrons.

If the assumption that the outer completed group of electrons is 8 (the **octet rule**) is maintained, then it must sometimes be assumed that atoms may be linked by single electrons instead of by pairs. For example, phosphorus pentachloride must be represented as shown, with two **singlet** links.

It is, however, frequently assumed that the octet rule does not necessarily apply to elements beyond the first three periods, and in some cases not even to these. the sulphur atom in SF_6, for example, may be surrounded by 12 electrons ($\ddot{S}.+6F\cdot$).

Types of linkage.—The examples given enable us to recognise three principal types of linkage:

(1) **Electrovalency,** in **polar compounds** (salts), is the result of a *transfer* of electrons from one atom to another to produce two oppositely charged **ions**, each with an independent existence. Between them there is no valency bond (in the ordinary sense) but only non-directed electrostatic forces. Each ion forms a complete atomic core, *i.e.*, its outer electron shell is the same as that of the inert gas nearest to it in the periodic system:



(2) **Covalency,** in **non-polar compounds** (not ionised) is due to *sharing*

of electrons between two atoms, each shared pair constituting an ordinary valency bond, four shared electrons a double bond, and six a triple bond. The substance consists of neutral **molecules**:

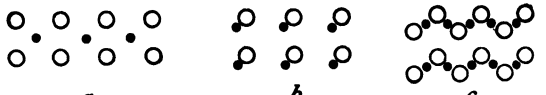
$$H^{\cdot} + {}^{\cdot}\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}}: = H:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}}:$$

(3) **Co-ordinate links**, or **semipolar double bonds**, are formed by pairs of electrons contributed by *one* of the atoms:

$$Cl_3B + :NH_3 \text{ give } Cl_3B \leftarrow NH_3$$

Another theory represents such compounds as $BCl_3.NH_3$ as formed from parts held together by electrostatic attraction—**residual affinity** (p 214).

Solid crystals may consist of (*a*) **ionic lattices** (salts); (*b*) **molecular lattices**, *e.g.*, *solid* O_2, N_2, CO, NO, $CH_3.CH_3$, in which the intermolecular forces (between the molecules) are different from the



a *b* *c*

FIG 237

intramolecular forces (between the atoms); these are usually non-conductors of electricity and relatively easily volatile; (*c*) **Layer lattices** made up of large ions each associated with two small ions forming practically electrically neutral layers held together by weak non-polar forces and easily split into thin sheets (*e.g.*, CdI_2, $Mg(OH)_2$, etc.) (Fig. 237); (*d*) **metals** and their compounds with one another: [Na], [Cu], [Cu_2Mg], perhaps [Pd_2H]; in which there is probably no difference between intermolecular and intramolecular forces; they are difficultly volatile, and conductors; (*e*) according to Grimm and Sommerfeld the solid elements standing four places before an inert gas in the periodic system, also certain compounds of neighbouring elements, form atomic lattices with tetrahedral linkages, as in the **diamond lattice** (p. 431):

[C] [Si] [CSi] [Ge] [Sn];
[AlN] [ZnS] [AgI];
perhaps [SiO_2] [Al_2O_3] [Si_3N_4] [P_3N_5];

these are mostly difficultly volatile, hard, and non-conductors; the electrons are redistributed to give a tetrahedral arrangement of atoms:

$$\begin{array}{cc} :\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}: & :\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Zn}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Zn}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}: \\ :\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}: & :\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Zn}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Zn}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}: \\ :\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}: & :\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Zn}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{Zn}}}:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}: \end{array}$$

(*f*) in crystals of solid argon or of other inert gas atoms the intermolecular forces are identical with the intramolecular forces, as in salts and metals, but are non-polar.

The distinction between **polar** (*dualistic*) and **non-polar** (*unitary*) compounds is evident from X-ray analysis (*e g.*, $\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{Cl}}$, diamond), by residual rays (p. 433); by the occurrence of optical activity or special kinds of stereoisomerism which necessitate directed valency bonds (non-polar), by considerations of colour, etc (*e g*, ionisation of a polar salt produces little change of colour). In polar compounds the sum of the outer electrons is 8 or a multiple of 8 (*e g.* $\overset{8}{\mathrm{Na}}\overset{8}{\mathrm{Cl}}$) but not in non-polar compounds ($\mathrm{F:F}$., *i.e*, 14).

Abegg distinguished the polar character of an element by (1) ionisation, *e g*, $\mathrm{HCl=H^+ + Cl^-}$, (2) hydrolysis, *e g*, $\mathrm{P_3N_5 + 12H_2O = 3H_3P^{+}O_4 + 5\overset{-}{N}\overset{+}{H}_3}$; (3) position in the periodic system as compared with that of other elements with which it combines, *e g*, $\overset{+}{\mathrm{S}}_2\overset{-}{\mathrm{Cl}}_2$, (4) the formulae of compounds in which it exerts its maximum valency. The last criterion is based on Abegg's theory that an element has a **normal valency** and a **contravalency**, the sum of which is equal to eight (p. 208)

Group	I	II	III	IV	V	VI	VII
Normal valency	+1	+2	+3	±4	−3	−2	−1
Contra-valency	(−7)	(−6)	(−5)		+5	+6	+7

E g., S in $\mathrm{H_2S^{2-}}$ and $\mathrm{S^{6+}O_3}$. If we represent the compound $\mathrm{BCl_3,NH_3}$ with a semipolar double bond, we see that the boron atom has a valency of −5.

Werner's Theory

Co-ordination compounds.—The formation of the compound $\mathrm{BF_3, NH_3}$ from the two molecules $\mathrm{BF_3}$ and $\mathrm{NH_3}$, neither possessing free valency in the usual sense, is explained (p 452) by the formation of a covalent bond between N and B by the donation of the lone pair of electrons of the nitrogen to form a co-ordinate bond (dative bond, semipolar double bond): $\mathrm{F_3B \leftarrow NH_3}$, a type of linkage believed to be exhibited in large groups of so-called **co-ordination compounds**, first systematised by Alfred Werner (1893).

The saturated molecules $\mathrm{PtCl_4}$ and $\mathrm{2HCl}$ combine to form a stable dibasic acid, $\mathrm{H_2PtCl_6}$, capable of ionisation and of forming salts such as $\mathrm{K_2PtCl_6}$, in which the chlorine is not ionisable but is firmly bound to the metal atom, silver nitrate, for example, giving not silver chloride but the salt $\mathrm{Ag_2PtCl_6}$. Werner represents $\mathrm{H_2PtCl_6}$ as

$$\mathrm{H_2\,[\overset{IV}{Pt}Cl_6] \rightleftharpoons 2H^{\cdot} + [\overset{IV}{Pt}Cl_6]''}$$

the group in square brackets forming a complex **nucleus**. The compound $\mathrm{PtCl_4}$ also combines with ammonia to form $\mathrm{PtCl_4(NH_3)_2}$, which

has no properties of a salt but behaves as a neutral molecule ; it gives no reactions for Pt or Cl′ ions and forms a non-conducting solution. It is an uncharged nucleus : $[PtCl_4(NH_3)_2]$. In the numerous stable compounds containing tervalent cobalt and ammonia (**cobaltammines**), and in the cobaltinitrites, the cobalt atom is also associated in the nucleus with six atoms, radicals, or neutral molecules :

$$(a)\ [\overset{III}{Co}(NH_3)_6]Cl_3 \rightleftharpoons [\overset{III}{Co}(NH_3)_6]''' + 3Cl',$$

$$(b)\ [\overset{III}{Co}(NH_3)_4Cl_2]Cl \rightleftharpoons [Co(NH_3)_4Cl_2]^{\cdot} + Cl',$$

$$(c)\ [\overset{III}{Co}(NO_2)_6]K_3 \rightleftharpoons 3K^{\cdot} + [Co(NO_2)_6]'''.$$

In the compound (*b*) only one-third of the chlorine is ionisable and exists as ions bound to the positive nucleus by electrostatic forces, like the ions in salts (p 428) . the rest of the chlorine is firmly bound to the metal atom in the nucleus by covalencies In a similar way, the ferro- and ferri-cyanides contain the cyanogen radicals attached by covalencies to the iron atoms in the nuclei and show none of the reactions of iron or cyanides :

$$K_4[\overset{II}{Fe}(CN)_6] \rightleftharpoons 4K^{\cdot} + [\overset{II}{Fe}(CN)_6]'''',$$

$$K_3[\overset{III}{Fe}(CN)_6] \rightleftharpoons 3K^{\cdot} + [\overset{III}{Fe}(CN)_6]'''.$$

In sodium nitroprusside one negative cyanogen radical is replaced in the ferricyanide by a neutral NO molecule, and the negative electrovalency of the nucleus is reduced from 3 to 2 : $Na_2[\overset{III}{Fe}(CN)_5NO]$.

Although in most cases the central atom in the nucleus is a metal, non-metallic compounds may similarly be represented :

$$\left[\begin{matrix}O & O\\ & P\\ O & O\end{matrix}\right]H_3 \quad \left[\begin{matrix}O & O\\ & P\\ O & H\end{matrix}\right]H_2 \quad \left[\begin{matrix}O & H\\ & P\\ O & H\end{matrix}\right]H \quad \left[\begin{matrix}O & O\\ & S\\ O & O\end{matrix}\right]H_2 \quad \left[\begin{matrix}S & O\\ & S\\ O & O\end{matrix}\right]H_2.$$

The atoms or radicals in the nucleus, **co-ordinated** with the central atom, since they are not ionisable must be attached by covalencies. The number of such groups, which is very often six, but may be four, as in the oxyacids of phosphorus and sulphur above, and sometimes eight, as in $[Mo(CN)_8]K_4 + 2H_2O$ and $[Mn(CN)_8]K_4$, is called the **co-ordination number.**

The metal in the compounds of tervalent cobalt and quadrivalent platinum exhibits the co-ordination number six ; bivalent platinum has the co-ordination number four.

$[Co^{III}(NH_3)_6]Cl_3$	$[Pt^{IV}(NH_3)_6]Cl_4$
$[Co^{III}(NH_3)_5H_2O]Cl_3$ *roseo*-salts	—
$[Co^{III}(NH_3)_5Cl]Cl_2$ *purpureo*-salts	$[Pt^{IV}(NH_3)_4Cl_2]Cl_2$ 2 forms
$[Co^{III}(NH_3)_4Cl_2]Cl$ *praseo*-salts	$[Pt^{IV}(NH_3)_3Cl_3]Cl$
$[Co^{III}(NH_3)_4(NO_2)_2]Cl$ 2 forms. *flavo*-salts, *croceo*-salts (NO_2 is the nitrite radical).	$[Pt^{IV}(NH_3)_2Cl_4]$ 2 forms $[Pt^{IV}(NH_3)Cl_5]K$
$[Co^{III}(NH_3)_3(NO_2)_3]$ 2 forms Gibbs's orange, Erdmann's orange	$[Pt^{IV}Cl_6]K_2$
$[Co^{III}(NH_3)_2(NO_2)_4]K$	$[Pt^{II}(NH_3)_4]Cl_2$ $[Pt^{II}(NH_3)_3Cl]Cl$ $[Pt^{II}(NH_3)_2Cl_2]$ 2 forms $[Pt^{II}(NH_3)Cl_3]K$ $[Pt^{II}Cl_4]K_2$
$[Co^{III}(NO_2)_6]K_3$	

The existence of isomeric forms of some types is mentioned.

That the formulae correctly represent the numbers of ions formed from the compounds is shown by the molecular conductivities at equal concentrations :

$[Co(NH_3)_6]Cl_3$ 4 ions ; 412	$[Co(NH_3)_5NO_2]Cl_2$ 3 ions ; 240	$[Co(NH_3)_4(NO_2)_2]Cl$ 2 ions ; 97
$[Co(NH_3)_3(NO_2)_3]$ no ions ; 1·5		
$[Co(NO_2)_6]K_3$ 4 ions ; 418	—	$[Co(NH_3)_2(NO_2)_4]K$ 2 ions ; 97

Valency rule for co-ordination compounds.—An examination of the formulae given above shows that *the electro-valency of the nucleus is equal to the positive valency of the metal or other central atom when this is co-ordinated only with saturated molecules such as* NH_3, H_2O *or* NO ; *but if negative radicals such as* Cl, NO_2, *or* CN, *which may be regarded as ions, are in the nucleus, the positive valency of the central atom is reduced by one unit for each univalent radical (or n units for*

each n-valent radical) present, and if the negative valency of these radicals exceeds the positive valency of the central atom, the nucleus as a whole becomes negative and is associated with a corresponding number of positive ions outside. For example :

$[\overset{IV}{Pt}(NH_3)_4Cl_2]$ has a valency of $4-2=2$ and forms

$$[\overset{IV}{Pt}(NH_3)_4Cl_2]Cl_2.$$

$[\overset{IV}{Pt}(NH_3)Cl_5]$ has a valency of $4-5=-1$ and forms

$$[\overset{IV}{Pt}(NH_3)Cl_5]K.$$

$[\overset{III}{Fe}(CN)_6]$ has a valency of $3-6=-3$ and forms

$$K_3[\overset{III}{Fe}(CN)_6].$$

$[\overset{II}{Fe}(CN)_6]$ has a valency of $2-6=-4$ and forms

$$K_4[Fe(CN)_6]$$

$[\overset{III}{Fe}(NO)(CN)_5]$ has a valency of $3-5=-2$ and forms

$$Na_2[Fe(NO)(CN)_6].$$

$[\overset{III}{Co}(SO_4)(NH_3)_5]$ has a valency of $3-2=1$ and forms

$$[Co(NH_3)_5SO_4]Br.$$

$[\overset{III}{Co}(NH_3)_5Br]$ has a valency of $3-1=2$ and forms

$$[Co(NH_3)_5Br]SO_4$$

The last two compounds are isomeric ; the first behaves in solution as a bromide, the second as a sulphate.

Positive and negative nuclei may also form salts with each other, *e.g.*, $[\overset{III}{Cr}(NH_3)_6]\cdot[\overset{III}{Cr}(SCN)_6]$, with valencies of $+3$ and -3, respectively.

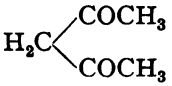
Chelate and dentate groups.—In some cases groups may occupy two, three, or four co-ordination positions, when they are known as chelate (Greek *chele*, a crab's claw), tridentate and quadridentate groups respectively :

(i) Chelate groups (2 positions) : ethylenediamine,

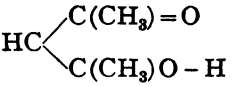
$$NH_2 . CH_2 . CH_2 . NH_2,$$

represented by en ; $\alpha\alpha'$-dipyridyl (dipy) ; radicals such as C_2O_4'', CO_3'', SO_3'', SO_4'', and the radicals of acetylacetone and dimethyl glyoxime. In the last two cases the group has one principal valency

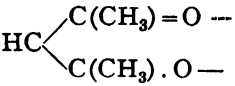
(due to loss of H from the compound) and one residual (secondary) valency, exerted by the oxygen and nitrogen, respectively, forming a co-ordination bond by donation of a lone pair of electrons to the shell of the central atom to which the group is attached :



I. Acetylacetone.



II. Monoenolic form.

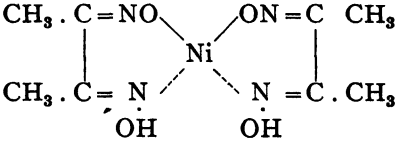


III. Chelate group.

Compounds of acetylacetone with elements having co-ordination numbers of 2, 4, 6 and 8 are known :

$$[\overset{I}{\mathrm{NaAc}}] \quad [\overset{II}{\mathrm{BeAc_2}}] \quad [\overset{III}{\mathrm{BAc_2}}]\cdot X' \quad [\overset{III}{\mathrm{AlAc_3}}] \quad [\overset{IV}{\mathrm{SiAc_3}}]\cdot X' \quad [\overset{IV}{\mathrm{ThAc_4}}]$$

Compounds with dimethylglyoxime include the important nickel dimethylglyoxime (p. 989) :



In this case it has been proved that the four valencies surrounding the metal atom are in one plane (Sudgen, 1932).

(ii) Tridentate groups (3 positions) : $\alpha\beta\gamma$-triaminopropane,

$$NH_2 . CH_2 . CH(NH_2) . CH_2 . NH_2, \quad (=\mathrm{tp}),$$

e.g., in $[\overset{III}{\mathrm{Co\ tp_2}}]Cl_3$, $[\overset{III}{\mathrm{Rh\ tp_2}}]Cl_3$ (Pope and Mann, 1925).

(iii) Quadridentate groups (4 positions) : ethylenediaminobisacetylacetone (a dienolic ketone), =ec ; *e.g.*, $[\overset{III}{\mathrm{Co\ ec}}(NH_3)_2]Br$ (Morgan and Smith, 1925) ; $\beta\beta'\beta''$-triaminopropane, $N(CH_2CH_2NH_2)_3$ = tren ; *e.g.*, $[\overset{II}{\mathrm{Ni}}(NH_3)_4]SO_4$, $[\overset{II}{\mathrm{Ni\ tren}}]SO_4$, $[\overset{II}{\mathrm{Pt\ tren}}]I_2$ (Mann, 1926).

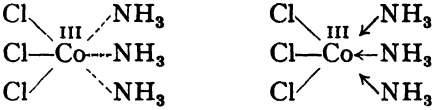
Electronic theory of co-ordination compounds.—Sidgwick (1923) postulates that : (i) Residual valencies, which behave as normal covalencies, are formed by the donation of a pair of electrons by an atom possessing a lone pair, such as nitrogen and oxygen, in the addenda (NH_3, H_2O, etc.), each bond so formed introducing two electrons to the shell of the central atom but not altering the electric charge, since the added molecule is neutral.

(ii) Electrovalencies are produced by such processes as the following : in $[\overset{IV}{\mathrm{Pt}}(NH_3)_2Cl_4]$, a neutral complex in which the atoms and

groups are united by covalencies, let the Cl be removed as an ion, taking one electron from the shell of the metal to form : $\dot{\underset{\cdot\cdot}{Cl}}$: and leaving a positive charge on the metal. The *pair* of electrons so lost is then supplied by donation from another NH_3 molecule added :

$$[Cl_3(NH_3)_2Pt \times \dot{\underset{\cdot\cdot}{Cl}} :] \; [Cl_3(NH_3)_2Pt]^+ + \times \dot{\underset{\cdot}{Cl}} : \; [Cl_3(NH_3)_2Pt : NH_3]^+.$$

In this example the Pt is surrounded by a shell of 12 electrons. We must, on this theory, represent the residual valencies by the symbol for the co-ordinate or semipolar bond :



It has otherwise been assumed that the links between the central atom and the addenda are formed by single electrons (singlet links), in which case outer groups of six electrons (sextets) would be formed with the co-ordination number six.

Isomerism of Complex Compounds.—Seven types of isomerism are predicted by Werner's theory :

(1) *Structural isomerism in the nucleus : e g* :

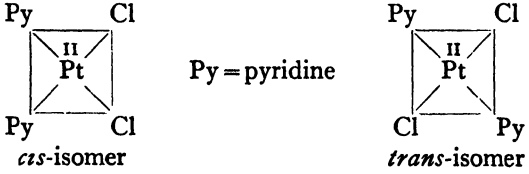
$$\left[\begin{matrix}NO—O\\NO—O\end{matrix} Co\ en_2\right] \text{ and } \left[\begin{matrix}O_2N\\O_2N\end{matrix} Co\ en_2\right].$$

(2) *Ionisation isomerism*, in which positions inside and outside the nucleus are interchanged, *e.g.*,

$$[Co(SO_4)(NH_3)_5]Br \text{ and } [CoBr(NH_3)_5]SO_4.$$

(3) *Geometrical isomerism*, due to the different arrangement of the atoms and groups in space about the central metal atom :

(*a*) In a plane square :



cis-isomer *trans*-isomer

In other cases the groups are arranged tetrahedrally about the central atom, as in the 4-covalent compounds of bivalent copper and zinc ; in compounds where the four groups attached to the metal in the ion $[MeR_4]^{\cdot\cdot}$ are different, the substance is optically active. Similar optically active compounds, well known with carbon, have been described for silicon, phosphorus, sulphur, selenium, arsenic and tin.

(*b*) Nuclei 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 six covalencies directed to the six corners (Fig. 238*a*). (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 com-

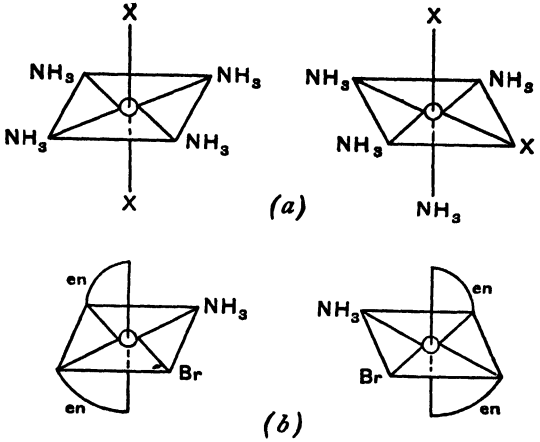


FIG 238.—Isomerism on Werner's theory.

pounds $[Co(NH_3)_4X_2]X$ are of this type. The *cis*-modifications are distinguished from the *trans*-modifications by their capacity for ring-formation.

The arrangement of four groups in a square around the central atom in such compounds as $K_2[\overset{II}{Pt}Cl_4]$ and $[\overset{II}{Pt}(NH_3)_4] \cdot [\overset{II}{Pt}Cl_4]$ (green salt of Magnus), and the octahedral arrangement of atoms or groups about the central atom in compounds such as I. $(NH_4)_2[PtCl_6]$, and II $[Ni(NH_3)_6]Cl_2$, have been confirmed by X-ray analysis (Wyckoff, 1921, etc.). In I. the structure of the lattice is the same as that of fluorspar, with the Ca ions replaced by $PtCl_6$ and F by NH_4 In II the NH_3 molecules are arranged about the Ni in the same way as the Cl atoms in $PtCl_6$ in I., and the two compounds are isomorphous.

(4) *Co-ordination isomerism*, depending on the different arrangements of groups in two nuclei in combination :

$[Cr(NH_3)_6]\cdot[Cr(SCN)_6]$ and $[Cr(NH_3)_4(SCN)_2]\cdot[Cr(NH_3)_2(SCN)_4]$.

(5) *Co-ordination polymerism* :

$[Cr(NH_3)_3(SCN)_3]$ 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*:

$[Cr(NH_3)_6]Cl_3 \rightarrow [Cr(H_2O)(NH_3)_5]Cl_3 \rightarrow [Cr(H_2O)_6]Cl_3$
ammine compound. *aquo-compound.*

In such compounds, part of the ionisable Cl may pass into the nucleus:

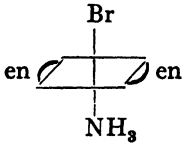
$$[Cr(H_2O)(NH_3)_5]Cl_3 = [CrCl(NH_3)_5]Cl_2 + H_2O.$$

It then ceases to be ionisable. The two green chromic chlorides (p. 934) are isomeric 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 compounds shown in Fig. 238*b* are two optically active *cis*-forms (the metal atom is in the centre of the square), and there is also one optically inactive *trans*-form:



The bivalent ethylenediamine group *en* in the *cis*-forms engages *two* valencies of the metal atom, one axial and one in the plane.

Co-ordination and valency.—Co-ordination often increases the stability of compounds in a marked degree. Whereas tervalent cobalt is unstable in its simple compounds, the cobaltammines are very stable substances. Cuprous nitrate forms a stable compound with methyl cyanide, $[\overset{I}{Cu}(CH_3CN)_4]NO_3$. Cupric iodide forms stable co-ordination compounds such as $[\overset{II}{Cu}(NH_3)_6]I_2$. Co-ordination compounds of bivalent silver, $[Ag(dipy)_3]X_2$, in which dipy = $\alpha\alpha'$-dipyridyl and X is a univalent cation (Morgan and Burstall, 1930) are paramagnetic, the molecular mass-susceptibility being equal to that of bivalent copper, showing that an electron has been extracted from an inner level of the silver atom (p. 469).

The quantum numbers.—The simplest atom, that of hydrogen, (At. No. 1) consists according to Bohr's theory of one electron of charge $-e$ rotating around a nucleus of charge $+e$, *i.e.*, a proton. First consider the orbits to be circles. If the nucleus were the sun

and the electron a planet subject to gravitational forces, *any* orbit would be possible, each with an appropriate kinetic energy of the planet which would keep it in that orbit against the pull of gravitation tending to drag it into the sun In the case of the proton and electron this is not possible, since the moving electron would give out radiation, gradually lose energy and fall spirally into the nucleus. Bohr assumed that there is now a limited number of " stationary " orbits, in each of which the electron rotates without radiation, whilst when it passes from one orbit to another it emits radiation according to the quantum equation (p. 448). If we imagine the electron starting at an infinite distance, it will pass into successive orbits each nearer the nucleus, giving off energy between each transition until it arrives at the smallest possible orbit, nearest the nucleus, when the atom is said to be in the *normal state.*

The whole series of possible orbits in this case is a series of circles with the nucleus at the centre. Each orbit is characterised by a **quantum number,** n, which determines the energy of the electron according to, and is itself defined by, the equation:

$$E_n = -Kh/n^2, \quad \ldots\ldots \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where K is a constant, having for the hydrogen atom the value:

$$K = 2\pi^2 e^4 m/h^3 = 3{\cdot}29 \times 10^{15}, \quad \ldots \quad \ldots\ldots \quad \ldots\ldots (2)$$

e and m being the charge and mass of the electron, and h Planck's constant. In passing from an orbit of quantum number n_1 to one of quantum number n_2, the energy given out is therefore:

$$E_1 - E_2 = \Delta E = Kh\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right), \quad \ldots\ldots\ldots\ldots\ldots (3)$$

and hence by the quantum equation, the frequency of the light emitted will be:

$$\nu = \Delta E/h = K\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right). \quad \ldots\ldots\ldots\ldots\ldots (4)$$

It is most important to notice that ν is *not* the frequency of revolution of the electron in its orbit, but is c/λ, where c is the velocity of light and λ the wave-length of the line in the spectrum corresponding with the transition of the electron from one orbit to another in the atom

When n_2 is given various small whole number values, such as 1, 2, 3; and n_1 given a series of higher whole number values (*e g*, $n_2 = 2$; $n_1 = 3, 4, 5, \ldots \infty$), equation (4) gives with great accuracy the frequencies (or wave-lengths) of the lines in the various spectral series of hydrogen (*e.g.*, with the values just quoted, the various lines of the **Balmer series,** four of which were mentioned on p. 152). Thus n is always a whole number (zero excluded), from 1 to infinity. K/n^2 is called a **term.**

If instead of consisting of a single proton of charge $+e$, the nucleus has a charge $+Ze$, and there is still a single electron of charge $-e$ rotating about it, the value of K in (4) is replaced by Z^2K, *e g*, for the singly ionised helium atom ($Z=2$), the spectra are given by equation (4) with $4K$ instead of K. This is true only when there is a single outer electron, since otherwise the electrons surrounding the nucleus exert a screening effect on its positive charge.

Still confining our attention to the hydrogen atom we may recall that the actual orbit of a planet round the sun is, according to Kepler's laws, an ellipse with the sun at a focus rather than a circle, and as well as circular electronic orbits we may also have a series of elliptical orbits, in each or several of which the electron has the same energy as in a corresponding circular orbit Each orbit will thus, by (1), be characterised by a **total quantum number** n, but each ellipse, for a given value of n, requires another number, k, for its definition, called a **subsidiary quantum number**. k has also whole number values (zero excluded). Very approximately, the ratio of the total to the subsidiary quantum number is that of the major to the minor axis of the ellipse. For the circular orbit this ratio is 1, and the orbit for which the principal and subsidiary quantum numbers are equal is always a circle.

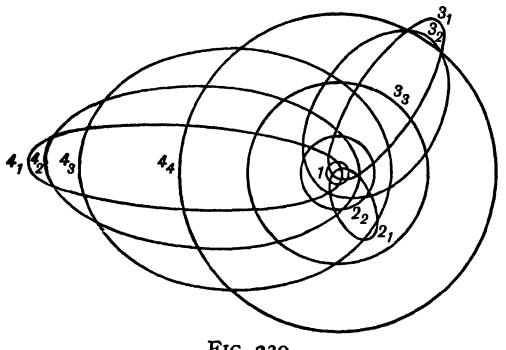


FIG. 239.

If we denote a particular orbit for which the two quantum numbers are n and k by n_k, the orbit n_n is always a circle For a total quantum number n, the quantum number k may have n values, viz., 1, 2, 3, ... n. For a principal quantum number 4 ($n=4$) we may have $k=1$, 2, 3, 4, and four possible orbits, viz , one circle 4_4, and three ellipses 4_1, 4_2 and 4_3, in which the ratios of the major to the minor axes are 4 : 1, 4 2 and 4 3, respectively. These orbits are shown in Fig. **239**, together with the 1_1, 2_1, 2_2; 3_1, 3_2, 3_3 orbits

Additional refinements appear in the spectrum of hydrogen as **fine structure**: each hydrogen line, previously regarded as single, really consists of two, very close together but visible with spectroscopic apparatus of high resolving power. To explain this requires a third quantum number, which defines the *spin* of the electron about its own axis, which gives the electron a moment of momentum and also a magnetic moment (since it acts as a circular current). Each of these

always has the same numerical value but the spin may be in one of two directions, so that this **spin quantum number,** s, may have two values only, which are found to be $+\frac{1}{2}$ and $-\frac{1}{2}$.

Owing to its spin about its axis, an electron has a magnetic moment A molecule containing an odd electron, *i.e.*, one which has not paired with another of opposite spin to form a covalency bond (p 475), will therefore exhibit paramagnetism (cf. pp 352, 469, 584 B)

The splitting of spectrum lines in a magnetic field (**Zeeman effect**) introduces a fourth, **magnetic quantum number,** m, which defines the angle between the plane of the electron orbit and the direction of the magnetic field.

In place of Bohr's k, the new quantum theory introduces a quantum number l, always 1 less than k Every electron in the atom is now characterised by definite values of *four* quantum numbers :

$n = 1, 2, 3, \ldots \infty$;
$l = 0, 1, 2, \ldots (n-1)$, corresponding with $k = 1, 2, 3, \ldots n$;
$s = +\frac{1}{2}, -\frac{1}{2}$.
m

The spin momentum of the electron and the momentum of the revolution of the electron in its orbit combine to give different values of an **inner quantum number,** j, and for an atom with one electron :

$$j = l \pm s = l \pm \tfrac{1}{2}.$$

For the smallest value of l, viz. 0, j is given only one value, $+\frac{1}{2}$, but for all higher values of l it has two values, corresponding with the doublet character of the spectral terms. The magnetic quantum number is given the possible values $-j \leqq m \leqq +j$, *i.e.*, $j, j-1, \ldots -j+1, -j$.

In an atom containing more than one outer electron an empirical rule called **Pauli's principle** holds good : in the same atom there cannot be two (or more) electrons having all four quantum numbers, n, l(or k), j and m, the same.

Let $n = 1$, then l has the single value 0, hence $j = +s = \frac{1}{2}$ has also only one value ; m, however, has two values $-j$ and $+j$, viz., $\pm\frac{1}{2}$, so that there can be *two* electrons having the principal quantum number 1, but only two.

For $n = 2$, we have two values of l, viz. 0, 1. For the first of these, $j = +\frac{1}{2}$; for the second $j = 1 - \frac{1}{2} = \frac{1}{2}$ and $j = 1 + \frac{1}{2} = \frac{3}{2}$. Corresponding with $j = \frac{1}{2}$, we have $m = +\frac{1}{2}$ or $-\frac{1}{2}$, and with $j = \frac{3}{2}$ we have for the values of m: $+j = +\frac{3}{2}$, $-j = -\frac{3}{2}$, $j - 1 = \frac{1}{2}$, $-j + 1 = -\frac{1}{2}$. Altogether there are 8 possible cases, as is most clearly seen in Table IV, so that there can be *eight* electrons of total quantum number 2, but only 8. Similarly, as the table shows, there can be 18 electrons of total quantum

number 3, and 32 of total quantum number 4. These numbers, 2, 8, 18, 32, are, however, precisely the numbers of the elements in the periods of the Mendeléeff table (p. 417).

An alternative magnetic quantum number m_l, defined by $m = m_l + s$ determines the possible orientations of the orbit in a magnetic field; its values are restricted by the condition that m_l has the values: $l, l-1, l-2, \ldots -(l-1), -l$, *i.e.*, $2l+1$ values in all.

Each of these values can, by Pauli's principle, be associated with *two* spin quantum numbers, viz $+\frac{1}{2}$ and $-\frac{1}{2}$, hence the maximum number of electrons in a sub-group is

$$2(2l+1) \quad \text{or} \quad 2(2k-1)$$

Level n_k	-	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4
$k-1=l$	-	0	0	1	0	1	2	0	1	2	3
Maximum number of electrons	2	2	6		2	6	10	2	6	10	14

The periodic table.—We can now go on to consider the significance of these results in the structure of the periodic table. For this purpose we consider the addition of successive *outer* electrons to a nucleus, the positive charge of which increases step by step in units from 1 to 92. The electrons inside the nucleus we do not consider at all, but regard the nucleus in each case as ready formed from the appropriate number of protons and electrons, as previously explained.*

For a nuclear charge of +1 (in all cases the unit charge e is understood) there can be one outer electron only, and we obtain the neutral hydrogen atom. This outer electron is in a 1_1 orbit. For a nuclear charge of +2 there are two outer electrons In all cases, for the *neutral* atom, the total number of outer electrons, however they are distributed, is equal to the nuclear charge. The table IV shows that these must move in 1_1 orbits ($n=1$, $l=0$; $\therefore k=1$ and n_k is 1_1). This arrangement is a particularly stable one, since helium resists all chemical agents and the atom has no magnetic or electric moment. On account of the higher nuclear charge, the two circular orbits are nearer the nucleus than the circular 1_1 orbit of hydrogen. Helium closes the first period, the number of which is equal to the principal (or total) quantum number $n=1$. We could not, in fact, have more than *two* electrons in an atom with $n=1$, as Pauli's principle shows.

* The neutral atom of atomic number Z is considered to be synthesised from the stripped nucleus of charge $+Ze$ by progressive capture and binding of electrons one by one At each stage, the last electron added finally occupies that orbit which is most stable with respect to the nucleus and the electrons already bound It was assumed by Bohr that although the addition of each electron affects the strength of the binding of all the electrons added before it, yet it leaves unchanged the quantum numbers which characterise their orbits.

TABLE IV. QUANTUM NUMBERS

n	1	2			3				
l	0	0	1		0	1		2	
j	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{5}{2}$
m	$+\frac{1}{2}\ -\frac{1}{2}$	$+\frac{1}{2}\ -\frac{1}{2}$	$+\frac{1}{2}\ -\frac{1}{2}$	$-\frac{1}{2}\ +\frac{1}{2}\ +\frac{3}{2}\ -\frac{3}{2}$	$+\frac{1}{2}\ -\frac{1}{2}$	$+\frac{1}{2}\ -\frac{1}{2}$	$-\frac{1}{2}\ +\frac{1}{2}\ +\frac{3}{2}\ -\frac{3}{2}$	$-\frac{1}{2}\ +\frac{1}{2}\ +\frac{3}{2}\ -\frac{3}{2}$	$-\frac{1}{2}\ +\frac{1}{2}\ -\frac{3}{2}\ +\frac{3}{2}\ +\frac{5}{2}\ -\frac{5}{2}$
m_l	0 0	0 0	0 0	$-1\ +1\ +1\ -1$	0 0	0 0	$-1\ +1\ +1\ -1$	0 0 $+1\ -1$	$-1\ +1\ -2\ +2\ +2\ -2$
	2	2	6		2	6		10	
	2	8			18				

n	4									
l	0	1		2		3				
j	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	$\frac{7}{2}$			
m	$+\frac{1}{2}\ -\frac{1}{2}$	$+\frac{1}{2}\ -\frac{1}{2}$	$-\frac{1}{2}\ +\frac{1}{2}\ +\frac{3}{2}\ -\frac{3}{2}$	$+\frac{1}{2}\ -\frac{1}{2}\ +\frac{3}{2}\ -\frac{3}{2}$	$-\frac{1}{2}\ +\frac{1}{2}\ -\frac{3}{2}\ +\frac{3}{2}\ +\frac{5}{2}\ -\frac{5}{2}$	$+\frac{1}{2}\ -\frac{1}{2}\ +\frac{3}{2}\ -\frac{3}{2}\ +\frac{5}{2}\ -\frac{5}{2}$	$-\frac{1}{2}\ +\frac{1}{2}\ -\frac{3}{2}\ +\frac{3}{2}\ -\frac{5}{2}\ +\frac{5}{2}\ +\frac{7}{2}\ -\frac{7}{2}$			
m_l	0 0	0 0	$-1\ +1\ +1\ -1$	0 0 $+1\ -1$	$-1\ +1\ -2\ +2\ +2\ -2$	0 0 $+1\ -1\ +2\ -2$	$-1\ +1\ -2\ +2\ -3\ +3\ +3\ -3$			
	2	6		10		14				
	32									

The helium electron configuration remains unchanged in all atoms up to uranium, and the outer electrons of the atoms of elements in the next period (II) begin a new "shell" with $n=2$. Lithium (At. No. 3) binds the third electron in a 2_1 orbit, *i.e*, a long ellipse, part of which passes very near the nucleus and inside the 1_1 orbits, but the other part is far distant from the nucleus (see Fig. 238), so that this electron can be fairly easily removed, leaving the lithium ion, Li^+, with the external helium configuration. In beryllium there are two outer electrons (*i e*, outside the 1_1 orbits), both probably in 2_1 orbits, since Pauli's principle allows two, and only two, of these ($n=2$; $l=0$ and $k=1$), and since beryllium is bivalent, both are valency electrons. With boron, the third electron must, therefore, go into a new orbit, which is a 2_2, and in carbon there are two electrons in 2_2 orbits ($n=2$, $l=1$; $\therefore k=2$) This can proceed, with nitrogen, oxygen and fluorine, until there are 6 electrons in 2_2 orbits, which is the maximum number, and we thus reach a total of eight electrons, *i.e*, 2 in 2_1 orbits and 6 in 2_2 orbits, added outside the helium configuration and forming the stable outer octet of neon Fluorine and oxygen atoms will tend to bind these extra electrons to reach the neon configuration, but since their nuclear charges are only $+7$ and $+6$, respectively, their ions (each with 8 outer electrons) will have one and two negative charges, respectively· $\bar{F}$, $\bar{\bar{O}}$, whereas neon, with a nuclear charge of $+8$, is neutral with its 8 outer electrons.

The next period (III) is characterised by the principal quantum number 3. Sodium, the first element, has one outer 3_1 electron in a long ellipse and more easily removed than that of lithium, since the 8 electrons of the neon configuration screen the positive nuclear charge to some extent. In magnesium there are two electrons in 3_1 orbits, and Pauli's principle shows that this group is now filled ($n=3$, $l=0$ $\therefore k=1$). With aluminium, the third electron goes in a 3_2 orbit; there can be six electrons in 3_2 orbits, and these are added till argon is reached, having a stable outer configuration of $2+6=8$ electrons. *All the inert gases except helium have an outer group of* 8 *electrons.*

With potassium the electron goes into a 4_1 orbit, since this electron is easily removed (giving K^+) and must, therefore, be in a long elliptic orbit. Thus ten 3_3 orbits are left empty for the time being. Calcium has two 4_1 electrons, corresponding with its valency. With scandium, however, the spectrum shows that owing to the increasing nuclear charge, electrons can be held in the inner levels which now begin to fill up so that the next electron added, in forming the scandium atom, goes into a 3_3 orbit.

The outer structure of argon, viz., $2/2\,.\,6/2\,.\,6$, now begins to fill up, and the scandium structure is $2/2\,.\,6/2\,.\,6\,.\,1/2$, this being derived from calcium, $2/2\,.\,6/2\,.\,6/2$, by the addition of an electron to an *inner* (3_3) level. This goes on until chromium is reached, when one of the

two outer 4_1 electrons drops back into a 3_3 level, which now contains 5 electrons. In manganese the 5 remain and the next electron goes into the 4_1 level (see the complete Table V of electronic structures).

Iron, cobalt and nickel have 6, 7 and 8 electrons in the 3_3 levels With copper another electron drops back from the outer 4_1 level, making $8+10=18$ in the 3_2 and 3_3 levels and 1 in the 4_1 outer level. The inner 3 levels now contain 18 electrons and Pauli's principle (Table IV) shows that they are complete This completed inner group of 18 electrons persists unchanged in all the remaining elements.

The apparently rather arbitrary arrangement of electrons in the elements Ti to Cu is required by the spectra and is also able to explain fairly satisfactorily the chemical and physical properties of the elements V, Cr, Mn, Fe, Co and Ni, viz. the arrest of the valency to *2* or its variation by *one* unit at a time (although V, Cr and Mn have very varying valencies, as shown below, these differ by one), the paramagnetism, the colour of the ions (supposed to be characteristic of

Element		Valencies				
Ti		2	3	4		
V		2	3	4	5	
Cr		2	3		6	(?)
Mn		2	3	4	6	7
Fe		2	3		6	
Co		2	3			
Ni		2	3	4		
Cu	1	2				

incomplete inner groups), the changes of direction in the X-ray spectra curves (Fig. 225) and the appearance of the first triad (Fe, Co, Ni). This filling up of incomplete inner levels was first suggested by Ladenburg (1920) and was explained by Bohr in the manner indicated. From copper to krypton the filling up of the 4_1 and 4_2 levels proceeds normally until with krypton these levels contain a total of $2+6=8$ electrons, and the period is completed. In the Cu^{++} ion, the inner level is incomplete and the ion is coloured (at least when hydrated).

A new period begins with rubidium, in which a 5_1 electron appears (easily removed, and in a long elliptic orbit), the 4_3 and 4_4 levels remaining empty. After strontium, with two 5_1 electrons, the next electron goes back to a 4_3 level in yttrium, and this level is gradually filled, reaching ten electrons in palladium, in which the 5_1 electron drops back. The 5_1 and 5_2 levels are filled up normally to a complete octet of $2+6=8$ with xenon, which closes the period. In the case of copper all the inner orbits, including the 3_3 circles, are filled but in the case of silver the 4_4 circles are empty.

TABLE V. ATOMIC

	At No	K	L		M			N				O					P						Q	
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	
H	1	1																						S
He	2	2																						S
Li	3	2	1																					S
Be	4	2	2																					S
B	5	2	2	1																				P
C	6	2	2	2																				P
N	7	2	2	3																				S
O	8	2	2	4																				P
F	9	2	2	5																				P
Ne	10	2	2	6																				S
Na	11	2	2	6	1																			S
Mg	12	2	2	6	2																			S
Al	13	2	2	6	2	1																		P
Si	14	2	2	6	2	2																		P
P	15	2	2	6	2	3																		S
S	16	2	2	6	2	4																		P
Cl	17	2	2	6	2	5																		P
A	18	2	2	6	2	6																		S
K	19	2	2	6	2	6	0	1																S
Ca	20	2	2	6	2	6	0	2																S
Sc	21	2	2	6	2	6	1	2																D
Ti	22	2	2	6	2	6	2	2																F
V	23	2	2	6	2	6	3	2																F
Cr	24	2	2	6	2	6	5	1																S
Mn	25	2	2	6	2	6	5	2																S
Fe	26	2	2	6	2	6	6	2																D
Co	27	2	2	6	2	6	7	2																F
Ni	28	2	2	6	2	6	8	2																F
Cu	29	2	2	6	2	6	10	1																S
Zn	30	2	2	6	2	6	10	2																S
Ga	31	2	2	6	2	6	10	2	1															P
Ge	32	2	2	6	2	6	10	2	2															P
As	33	2	2	6	2	6	10	2	3															S
Se	34	2	2	6	2	6	10	2	4															P
Br	35	2	2	6	2	6	10	2	5															P
Kr	36	2	2	6	2	6	10	2	6															S
Rb	37	2	2	6	2	6	10	2	6	0	0	1												S
Sr	38	2	2	6	2	6	10	2	6	0	0	2												S
Y	39	2	2	6	2	6	10	2	6	1	0	2												D
Zr	40	2	2	6	2	6	10	2	6	2	0	2												F
Nb	41	2	2	6	2	6	10	2	6	4	0	1												D
Mo	42	2	2	6	2	6	10	2	6	5	0	1												S
Ma	43	2	2	6	2	6	10	2	6	6	0	1												D
Ru	44	2	2	6	2	6	10	2	6	7	0	1												F
Rh	45	2	2	6	2	6	10	2	6	8	0	1												F
Pd	46	2	2	6	2	6	10	2	6	10	0	0												S

Structures of the Elements

	At. No	K	L		M			N				O					P						Q	
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	
Ag	47	2	2	6	2	6	10	2	6	10	0	1												S
Cd	48	2	2	6	2	6	10	2	6	10	0	2												S
In	49	2	2	6	2	6	10	2	6	10	0	2	1											P
Sn	50	2	2	6	2	6	10	2	6	10	0	2	2											P
Sb	51	2	2	6	2	6	10	2	6	10	0	2	3											S
Te	52	2	2	6	2	6	10	2	6	10	0	2	4											P
I	53	2	2	6	2	6	10	2	6	10	0	2	5											P
Xe	54	2	2	6	2	6	10	2	6	10	0	2	6											S
Cs	55	2	2	6	2	6	10	2	6	10	0	2	6	0	0	0	1							S
Ba	56	2	2	6	2	6	10	2	6	10	0	2	6	0	0	0	2							S
La	57	2	2	6	2	6	10	2	6	10	0	2	6	1	0	0	2							D
Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1	0	0	2							H
Pr	59	2	2	6	2	6	10	2	6	10	2	2	6	1	0	0	2							K
Nd	60	2	2	6	2	6	10	2	6	10	3	2	6	1	0	0	2							L
Il	61	2	2	6	2	6	10	2	6	10	4	2	6	1	0	0	2							L
Sa	62	2	2	6	2	6	10	2	6	10	5	2	6	1	0	0	2							K
Eu	63	2	2	6	2	6	10	2	6	10	6	2	6	1	0	0	2							H
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1	0	0	2							D
Tb	65	2	2	6	2	6	10	2	6	10	8	2	6	1	0	0	2							H
Ds	66	2	2	6	2	6	10	2	6	10	9	2	6	1	0	0	2							K
Ho	67	2	2	6	2	6	10	2	6	10	10	2	6	1	0	0	2							L
Er	68	2	2	6	2	6	10	2	6	10	11	2	6	1	0	0	2							L
Tu	69	2	2	6	2	6	10	2	6	10	12	2	6	1	0	0	2							K
Yb	70	2	2	6	2	6	10	2	6	10	13	2	6	1	0	0	2							H
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1	0	0	2							D
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2	0	0	2							F
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3	0	0	2							F
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4	0	0	2							D
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5	0	0	2							S
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6	0	0	2							D
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7	0	0	2							F
Pt	78	2	2	6	2	6	10	2	6	10	14	2	6	9	0	0	1							F
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	1							S
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2							S
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	1						P
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	2						P
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	3						S
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	4						P
Eka I	85	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	5						P
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6						S
Eka Cs	87	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	0	0	0	0	1	S
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	0	0	0	0	2	S
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	1	0	0	0	2	D
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	2	0	0	0	1	H
U-X	91	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	4	0	0	0	1	K
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	5	0	0	0	1	L

In the period beginning with caesium a 6_1 electron is added, in barium two 6_1 electrons. From and including lanthanum, however, the valencies remain constantly 3 until the last rare-earth element, lutecium, is reached, the electrons going to complete the empty 4_4 orbits deep within the atom To the eighteen electrons of orbits of principal quantum number 4 there are now added in succession fourteen more, making up a total of 32, the maximum possible for this quantum number ($n=4$) Since all these electrons are well within the stable octet completed in xenon they have no appreciable influence on the chemical properties, which remain practically constant, and thus both the number (15) and chemical properties of the rare-earth elements in this period (sometimes called **lanthanides**, to distinguish them from the total number of rare-earth elements, which includes scandium and yttrium in earlier periods), are explained by Bohr's theory.

The element following lutecium cannot, therefore, be a rare-earth element as was formerly supposed but must, as Bohr pointed out, be a fourth group element related to zirconium. This was completely confirmed by the examination of the properties of hafnium, newly discovered by Coster and Hevesy (p. 413). Just as was the case in the fourth and fifth periods, the rearrangement of electrons in the rare-earth elements is accompanied by the appearance of coloured ions and paramagnetism.

In the following elements as far as gold, the 5_1 and 5_2 levels of xenon, containing 8 electrons, are completed by the addition of ten electrons to the 5_3 levels, making up a total of 18, whilst with gold the 6 levels begin to fill up, leading to the completion of the 6_1 and 6_2 levels with $2+6=8$ electrons, forming the outer shell of the inert gas, the emanation. In the remaining elements of the fragmentary period, after a missing element in the first group, the 7_1 level in radium has two electrons. The 6_3 levels begin to fill up with actinium, but when five electrons have occupied 6_3 orbits we reach, for some reason not known, the end of the elements with uranium.

If we now look back over the path which has led to this view of the Periodic System, we notice that each period is characterised by a total quantum number, n, of the outer electrons, one unit higher than in the preceding inert gas, and that n is equal to the number of the period. *E.g.*, the outer electron in potassium is in a 4_1 orbit, those of argon in 3_1 and 3_2 orbits, whilst the period number for potassium (p. 411) is 4. All electrons with the same n are arranged in **groups** or " shells," each shell being fully occupied when it contains $2n^2$ electrons (2, 8, 18 or 32). These groups are divided into **subgroups** defined by the subsidiary quantum number k, or (on the modern theory) by the quantum number $l(k=l+1)$. The number of electrons in each completed subgroup is $2(2k-1)=4l+2$, *i.e.*, 2, 6, 10 and 14

for $l=0, 1, 2, 3$, or $k=1, 2, 3, 4$. This relation, introduced by Stoner (1924) from a consideration of the number of Zeeman terms into which the alkali-metal spectrum terms are split by a magnetic field, and simultaneously by Main Smith on chemical grounds, is in agreement with Pauli's principle.

Table of atomic structures.—Table V gives the distribution of electrons in the various levels (n_k) of all the known atoms The nomenclature of the levels at the top (*K*, *L*, *M*, .) is based on X-ray spectrum practice (p 434), the normal terms (*S*, *P*, *D*, *F*) at the side are based on optical spectrum notation, and are given for completeness although we shall not use them. Some minor differences of opinion exist as to the electron configurations of some of the more complex atoms, *e g* , the rare earth elements may contain one 6_1 and two 5_3 electrons instead of one 5_3 and two 6_1 electrons as given; and also the atoms of some elements in Group VIII *a* may exist in two slightly different configurations. These are shown in the tables at the beginning of the chapters dealing with the separate elements. On the whole, however, there is general agreement as to the data in the table.

A simpler table is Table VI (due to Roy Gardner), in which all elements having the same complete groups (that is, all stable groups of 2, 8, 18 or 32), are placed in the same horizontal row, and the vertical columns include elements with the same number of electrons in the incomplete outer groups. An asterisk marks elements for which the "normal" atom is thought to have only one electron in the outermost group, but practically all these give bivalent ions. The electronic arrangements are read off as shown by the following examples:

Sb 2 ; 8 ; 18 ; 18 ; 5.
Fe 2 ; 8 ; 14 ; 2.
Ce 2 ; 8 , 18 , 19 , 9 ; 2.

The existence of four types of elements is emphasised: (1) those with all groups complete; (2) those with one incomplete group; (3) those with two incomplete groups (transition elements); (4) those with three incomplete groups (rare earth elements). The upper limits of existence of covalencies of 8, 6, and 4 are marked by heavy horizontal lines.

Variable valency.—In order to explain the different valencies exhibited by some atoms it is necessary to consider the division of the valency electrons into sub-groups by means of the third quantum number. The group with $l=1$, as seen in Table IV, has two sub-groups with $j=\frac{1}{2}$ and $j=\frac{3}{2}$; that with $l=2$ has two sub-groups with $j=\frac{3}{2}$ and $j=\frac{5}{2}$; that with $l=3$ has two sub-groups with $j=\frac{5}{2}$

and $j=\frac{7}{2}$. Each sub-group is further subdivided into grouplets, and the maximum numbers of electrons in the sub-groups with $j=\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ and $\frac{7}{2}$ are 2, 4, 6 and 8 respectively.

TABLE VI.

	0	1 2 3 4 5 6 7	2 2 2 2 2 2 2 2 2	2 2 - 2 2
			9 10 11 12 13 14 15 16 17	9 9 - 9 9 19 20 - 30 31
		H		
2	He	Li Be B C N O F		
2 8	Ne	Na Mg Al Si P S Cl		
2 8 8	A	K Ca		
2 8			Sc Ti V Cr* Mn Fe Co Ni Cu*	
2 8 18		Zn Ga Ge As Se Br		
2 8 18 8	Kr	Rb Sr		
2 8 18			Yt Zr Nb* Mo* Ma* Ru* Rh* Pd* Ag*	
2 8 18 18		Cd In Sn Sb Te I		
2 8 18 18 8	X	Cs Ba		
2 8 18 18			La	
2 8 18				Ce - - Yb
2 8 18 32			Lu Hf Ta W Re Os Ir Pt Au*	
2 8 18 32 18		Hg Tl Pb Bi Po —		
2 8 18 32 18 8	Em	— Ra		
2 8 18 32 18			Ac Th* U*	

The different valencies (polar and non-polar) of elements preceding inert gases in the Periodic System, as shown in the Table VII, usually differ by 2 or multiples of 2, and this regularity also appears in the subdivision of the sub-groups of the completed electron shells. The sign + in the valency numbers denotes loss or sharing of electrons, the sign − gain of electrons Lead for example is bi- and quadrivalent, because its atom has two electrons with $l=0$ and $j=\pm\frac{1}{2}$, and two with $l=1$ and $j=\pm\frac{1}{2}$. (These are shown as 6_1 and 6_2 electrons, *i.e.*, with $k=1$ and $k=2$ in Table V; $l=k-1$) In $PbCl_2$ the two $n_{1\frac{1}{2}}$ electrons are removed, whilst in $PbCl_4$ the two $n_{0\frac{1}{2}}$ electrons are in addition removed or shared. The symbol n_{lj} denotes the electron with principal quantum number n, subsidiary (series) quantum number l, and inner quantum number j.

TABLE VII. VARIABLE VALENCIES.

Group	Element $n=2$	3	4	5	6	Valencies			
VII	(F)	Cl	Br	I	—	−1	+3	+5	+7
VI	(O)	S	Se	Te	(Po)	−2	2	4	6
V	N	P	As	Sb	Bi			3	5
IV	C	Si	Ge	Sn	Pb			2	4
III	(B)	(Al)	(Ga)	In	Tl			1	3
	Unshared electrons - -					4 2 2	0 2 2	0 0 2	0 0 0
						$n_{1\frac{3}{2}}$	$n_{1\frac{1}{2}}$	$n_{0\frac{1}{2}}$	

The figures on the last line denote the numbers of unshared $n_{1\frac{3}{2}}$, $n_{1\frac{1}{2}}$ and $n_{0\frac{1}{2}}$ electrons respectively, in this order, *e g.*, when Pb is exhibiting the valency 2 it has no $n_{1\frac{1}{2}}$ electrons but two $n_{0\frac{1}{2}}$ electrons; when it exhibits the valency 4 it has also lost or shared the $n_{0\frac{1}{2}}$ electrons. Chlorine has the valencies 1, 3, 5, 7, and in salts such as KCl, −1. The atom (as seen from Table IV) has three $3_{1\frac{3}{2}}$ (*i e*, one less than the number 4 for a completed group), two $3_{1\frac{1}{2}}$ and two $3_{0\frac{1}{2}}$ electrons, which are shared in 3-, 5- and 7-valent chlorine. Since in the neutral atom there is room for one $3_{1\frac{3}{2}}$ electron in the outer orbit to complete an inert gas configuration, this may be taken up as a polar valency of −1 Chlorine may also exhibit valencies of +1 and +4, as in Cl_2O and ClO_2, and these are explained as due to an electro-isomeric atom which has four $3_{1\frac{3}{2}}$, one $3_{1\frac{1}{2}}$ and two $3_{0\frac{1}{2}}$ electrons. In chlorine with a valency +1, the one $3_{1\frac{1}{2}}$ electron, and in chlorine with valency +4, the four $3_{1\frac{3}{2}}$ electrons, are given up or shared. The existence of this electro-isomeric atom is confirmed spectroscopically.

If we introduce the fourth quantum number (for the electron spin), *i.e.*, consider n, l, m and s, then for given values of n, l and m there are *two* values of s, viz., $+\frac{1}{2}$ and $-\frac{1}{2}$. This corresponds with the completion of grouplets of *two* electrons of opposite spins; the number is limited to two by Pauli's principle. These pairs are present in single atoms, and if an atom has one unpaired spin ($\rightarrow$) it may pair with another atom having an unpaired spin of the opposite sign ($\leftarrow$) to form a completed grouplet ($\rightleftarrows$). The way in which this is effected is difficult to describe: it is an exchange or resonance effect in terms of wave-mechanics which cannot be followed out in detail here, but this exchange energy makes possible the formation of a non-polar bond, and it in turn depends on the electron spins. On London's theory, the number of groups containing *unpaired* electrons gives the non-polar valency of an atom, because each is capable of forming a pair of electrons of opposite spin.

Table VIII shows the application of this rule to the first three periods. In the case of carbon, the atom has four valency electrons (the pair of electrons with $l=0$, *i.e.*, $k=1$, are in the inner shell completed with helium, and are not valency electrons), viz., those with $l=1$, of which (since $n=2$) four are possible with $j=\frac{3}{2}$, viz., those with

$$m=-\tfrac{1}{2},\ +\tfrac{1}{2},\ -\tfrac{1}{2}\ \text{and}\ +\tfrac{1}{2},$$

respectively In the table the values of m_l, the magnetic quantum number are given, where $m=m_l+s=m_l\pm\frac{1}{2}$, subject to the condition that $-l\leq m_l\leq +l$. The first equation gives for the values of m_l:

$$(s=-\tfrac{1}{2})\ -\tfrac{3}{2}-\tfrac{1}{2},\ +\tfrac{3}{2}-\tfrac{1}{2},\ -\tfrac{1}{2}-\tfrac{1}{2},\ +\tfrac{1}{2}-\tfrac{1}{2},\ i.e.,\ -2,\ +1,\ -1,\ 0,$$

$$(s=+\tfrac{1}{2})\ -\tfrac{3}{2}+\tfrac{1}{2},\ +\tfrac{1}{2}+\tfrac{1}{2},\ -\tfrac{1}{2}+\tfrac{1}{2},\ +\tfrac{1}{2}+\tfrac{1}{2},\ i.e.,\ -1,\ +2,\ 0,\ +1$$

Of the values -2, -1, 0, 1, 2, however, only -1, 0, $+1$ are permitted by the second condition, since l has the value $+1$. Hence m_l has only the values -1, 0 and $+1$.

Carbon, as we see by comparison with the completed shells in neon, may have two unpaired electrons (1 1) which can become paired (2 2) in the neon structure (viz, those for which $l=1$, and $m_l=-1$ and 0), or four such (1 1 1 1, for one of which $l=0$, $m_l=0$, and for three of which $l=1$ and m_l is -1, 0 and $+1$). Hence carbon is two or four covalent

It may be noted that oxygen can be only two covalent, so that in oxonium compounds in which it appears to have a valency of four it must, on this scheme, have two polar valencies, *e.g.*, $H_2O+HCl=H_3ClO=H_2\overset{+}{O}+\overset{-}{Cl}$. Nitrogen is limited to a maximum covalency of three, so that five valencies can appear only in polar compounds, *e.g.*, $NH_3+HCl=NH_4^++Cl^-$.

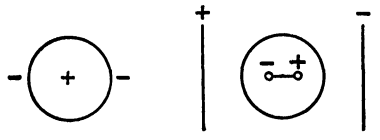
Ionising potentials.—If the electrons in a stream emitted from a hot filament in a gas at very low pressure are passed through a fall of potential V, as in the " grid " of a wireless valve, they will make collisions with gas atoms or molecules in their path. When the speed of the electrons is small, these collisions are elastic. If V is continually increased, a point is reached when the speed of the electron of charge e gives it an energy $\frac{1}{2}mv^2=eV$, such that it makes an inelastic collision with the atom of gas, giving up its energy to one of the outer electrons and so raising it to a higher quantum orbit. A critical value of V is reached when the colliding electron gives so much energy to the electron in the atom that the latter is completely removed, *i.e.*, ionisation occurs, *e.g.*, $K=K^++e$. The values of the ionising potential may be found directly as described, or more accurately by calculation from spectroscopic data. The values of the potentials (in volts) for the removal of successive electrons show that the valency electrons are relatively easily removed: H 13·53; Li 5·4, 75·3; C 11·2, 24·3, 47·7, 64·1, 400; O 13·6, 35, 55, 77, 109, 137·5 (733); P 11, 20, 30, 50, 65;

Table VIII. Non-Polar Valencies.

At No		Non-polar valency	1	2				3								n
			0	0	1			0	1			2				l
			0	0	−1	0	1	0	−1	0	1	−2	−1	0	1	2	m_l
1	H	1	1													
2	He	0	2													
3	Li	1	2	1												
4	Be	0	2	2												
		2	2	1	1											
5	B	1	2	2												
		3	2	1	1	1										
6	C	0	2	2	2											
		2	2	2	1	1										
		4	2	1	1	1	1									
7	N	1	2	2	2	1										
		3	2	2	1	1	1									
8	O	0	2	2	2	2										
		2	2	2	2	1	1									
9	F	1	2	2	2	2	1									
10	Ne	0	2	2	2	2	2									
11	Na	1	2	2	2	2	2	1								
12	Mg	0	2	2	2	2	2	2								
		2	2	2	2	2	2	1	1							
13	Al	1	2	2	2	2	2	2	1							
		3	2	2	2	2	2	1	1	1						
14	Si	0	2	2	2	2	2	2	2							
		2	2	2	2	2	2	2	1	1						
		4	2	2	2	2	2	1	1	1	1					
15	P	1	2	2	2	2	2	2	2	1						
		3	2	2	2	2	2	2	1	1	1					
		5	2	2	2	2	2	1	1	1	1	1				
16	S	0	2	2	2	2	2	2	2	2						
		2	2	2	2	2	2	2	2	1	1					
		4	2	2	2	2	2	2	1	1	1	1				
		6	2	2	2	2	2	1	1	1	1	1	1			
17	Cl	1	2	2	2	2	2	2	2	2	1					
		3	2	2	2	2	2	2	2	1	1	1				
		5	2	2	2	2	2	2	1	1	1	1	1			
		7	2	2	2	2	2	1	1	1	1	1	1	1		
18	A	0	2	2	2	2	2	2	2	2	2					
		2	2	2	2	2	2	2	2	2	1	1				
		4	2	2	2	2	2	2	2	1	1	1	1			
		6	2	2	2	2	2	2	1	1	1	1	1	1		
		8	2	2	2	2	2	1	1	1	1	1	1	1	1	

Cl 13, 24, 40, 47, 68, 89, 114 ; V 6·75, 14·7, 30, 48, 69, 120 ; Br 12, 20, 25 ; I 10·4 ; S 10·3, 23, 35, 47 , Se 9·7 ; Te 9.

Polar molecules.—There is evidence that the outer electron shells of atoms, molecules and ions are *deformable* under the influence of neighbouring charges. Neutral atoms placed in an electric field will generally be polarised, owing to the motion of the electron shell relative to the core, so that the centres of gravity as it were of the two charges no longer coincide, and an **induced dipole** consisting of a positive and negative doublet will be produced in the atom (Fig. 240).



a *b*

FIG 240.—Deformation of charges to produce an induced dipole

The field produced by a charged ion in a crystal may be about 10^3 volts per cm., and is thus capable of producing deforming effects on neighbouring ions. A measure of the *polarisability* of an atom, molecule or ion may be obtained by measurement of the refractive index, and in this way also ionic radii may be calculated.

Ions in solution will also tend to produce dipoles in the solvent molecules, so that the latter will arrange themselves around the ion with the axes of the dipoles towards the centre of the ion and the charge of the dipole opposite to that of the ion pointing towards it. An ion in water, for example, is surrounded by such a sheath of polarised water molecules, which it drags about with it in the solution (see p. 260).

In some cases the molecule contains a **permanent dipole**, due to a separation of charges and not merely produced by temporary deformation in an electric field. Such molecules are known as **polar molecules** and generally show peculiar properties. When they are liquids they usually: (i) are associated, (ii) have abnormally high boiling points, (iii) have high dielectric constants, (iv) are good ionising solvents. Whereas many of the properties of mixtures of **non-polar** liquids (such as benzene and other hydrocarbons) are almost additively composed of those of their constituents, those of mixtures of polar substances (such as water and sulphuric acid) deviate largely from this rule, and in addition there is usually a considerable heat of admixture. As regards the solvent action of the two classes of liquids, it is found that members of each one group are freely miscible with one another but not with members of the other group. With solids, it is found that non-polar substances usually have low melting points unless they have high molecular weights, whilst polar solids such as salts have high melting points. Some non-polar solids such as diamond have high melting points, but are probably atomic lattices. Non-polar solids are often more volatile than salts.

The value of the **dipole moment** of a molecule, *i.e.*, the charge at one end of the dipole multiplied by the distance between the equal and opposite charges, gives an indication as to whether the valency electrons are equally shared between the atoms : a pure covalent link, in which each atom contributes an equal charge and the electron pair is equidistant from the two cores, will have no dipole moment, but when the pair is drawn closer to one core, owing to the large positive charge of the latter, or for some other reason, then a permanent dipole moment will appear :

$$H : H \quad \text{No dipole moment} \qquad \overset{+}{H} : \overset{-}{Cl} \quad \text{Dipole moment}$$

The values of the dipole moments of some molecules, all gaseous except CCl_4 and $AgClO_4$ which are dissolved in benzene, are given in the table below in electrostatic units $\times 10^{18}$

Ethane - C_2H_6	0	N_2	0	HCl	1·034
Ethylene - C_2H_4	0	CO_2	0	HBr	0 788
Acetylene - C_2H_2	0	CCl_4	0	HI	0 382

NH_3	1·50
H_2O	1 8
$AgClO_4$	4 7

Distinctively non-polar molecules have zero dipole moment ; those in which a shift of electron pairs (covalencies) occurs (HCl, etc) have a small moment , salts ($AgClO_4$), and compounds containing semi-polar double bonds, in which electron transfer has occurred, have high moments unless some other compensating effect intervenes

The effect of the solvent on ionisation of a solute was referred by J. J. Thomson and by Nernst to the **dielectric constant.** The force between two charges at a distance d in a medium of dielectric constant D is e_1e_2/Dd^2, so that the attraction tending to bind two ions together is weaker the higher the value of D. Water, hydrocyanic acid and acetonitrile (CH_3CN) are good ionising solvents , the alcohols are medium ionising solvents, and benzene is a poor ionising solvent, as would be expected from the values of D given below :

Water - - - -	81	Ethyl alcohol - -	26
HCN - - - -	116	Sulphur dioxide (liq) -	13·75
CH_3CN - - -	39	Benzene - - -	2·29
Methyl alcohol - -	35		

Mutual deformation of ions.—Refraction measurements show that the electron shells of anions and of water molecules are less deformable when they are in close proximity to cations. The action of anions on cations is small, since the cations are usually smaller and less deformable. The deformability of an anion increases with increasing radius and charge ; the deforming action of cations increases with increasing charge and decreasing radius.

Some interesting speculations as to the colour of inorganic compounds follow from these considerations If we consider the salts in the following table, formed from the cations in the vertical row and

the anions in the horizontal row, also cations combined with water and ammonia, we may ascribe the increasing depth of colour in the series fluoride to iodide as due to the increasing deformability of the anion, which is increasing in size. Sulphates have the same colour as the fluorides (with a small anion) because the O^{--} ions in SO_4^{--} are relatively fixed owing to the binding forces rendering them less deformable, whilst the oxides themselves, with more deformable O^{--} ions, are much darker in colour. According to Fajans, the blue colour of hydrated cupric salts is (at least in part) due to the deformation of water molecules.

	F	Cl	Br	I	O	S	SO_4	H_2O	NH_3
Ni^{++} -	Yellowish	Yellow-brown	Dark brown	Black	Dark green	Black	Grey-blue	Green	Blue
Cu^{++} -	White	Yellow-brown	Brown-black	—	Black	Blue-black	White	Blue	Blue
Ag^{+}	Yellow	White	Yellow-white	Yellow	Dark brown	Black	White	Colourless	Colourless

Fajans has pointed out that the tendency to form polar or non-polar compounds is also related to the deformability of the electron shells Let a positive and negative ion be brought close together. If the deformation of the electron shells reaches such a magnitude that there is an actual transfer of electrons, then a non-polar compound will be formed. This will depend on the attraction exerted by the positive ion on the electrons of the negative ion and on the firmness with which the latter are held The attraction of the positive ion increases with its charge and also is larger when the ion is small, so that the negative ion may approach nearer the charge of the positive ionic core. The ease with which electrons are detached from the negative ion increases with its size, since then the outer electrons, being further from the positive core, are less firmly held Hence the conditions for the formation of polar and non-polar compounds may be summarised as follows :

Polar	Non-Polar
Positive charge low.	Positive charge high.
Large cation.	Small cation.
Small anion.	Large anion.

There are many apparent exceptions to Fajans' rule : mercuric chloride, for example, is not appreciably conducting in the fused state, although it should be a polar compound. This may be due to association.

The number of negative, as compared with positive, *atomic* ions is small : in solutions and crystals only the following occur :

H^- (*e.g.*, in LiH), F^-, Cl^-, Br^-, I^-, O^{--}, S^{--}, Se^{--}, Te^{--}, Po^{--},

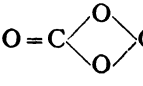
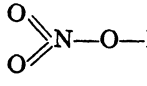
and they are known only with external configurations of 8 electrons; those with several valencies do not occur. The reason for the small number is supposed to be related to the tendency of anions with

increasing charge to leave the polar state on account of their greater deformability, although considerations as to the energy changes in the formation of anions and cations are also of importance.

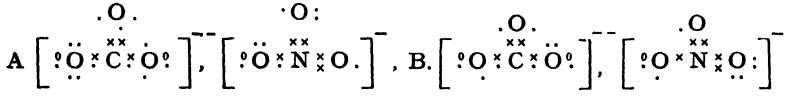
According to V. Goldschmidt (1926) the distances between the atoms in polyatomic ions in crystals depends to an appreciable extent on the nature of the other ions in the lattice *E g*, the distance N—O in the NO_3^- ion is 1·40 A.U in $NaNO_3$ and 1·15 A.U. in $LiNO_3$, because the small Li^+ ion has a stronger polarising effect on the NO_3^- ion than has the larger Na^+ ion In a similar way the TiO_3 complex in $CaTiO_3$ is expanded when Ca^{++} is replaced by the smaller Mg^{++}, and the resulting structure is very similar to $AlAlO_3$, the Mg and Ti being approximately equidistant from the nearest oxygen atoms In some cases a rearrangement of the atoms around the polarising ion may occur, as when the small Be^{++} ion replaces Ca^{++} in spinel, $CaAl_2O_4$, when the ions Ca^{++} and $[Al_2O_4]^{--}$ are converted into $[BeO_4]^{6-}$ and $2Al^{3+}$. It is even suggested, on the basis of X-ray experiments, that ammonium fluoride crystals do not, like other ammonium salts, consist of NH_4^+ and X^- [X^- = halogen ion] but of $NH_3 + HF$, owing to the deforming action of the small F^- ion on the NH_4^+ ion

Atomic structure and crystal structure.—According to Grimm (1921) isomorphous substances form mixed crystals when . (1) the chemical type is the same (*e g.*, NaCl, PbS , $BaSO_4$, $KMnO_4$) , (2) the lattice types of the crystals are the same ; (3) the atomic or ionic distances in the crystals are "similar," the necessary degree of similarity depending on the temperature and on the type of linking.

The isomorphism of many substances offered difficulty from the point of view of the old structural formulae, which indicated different constitutions for pairs of isomorphous compounds, *e g.* .

 for $CaCO_3$  for $NaNO_3$

From the point of view of crystal structure this difficulty would disappear if the *ions* CO_3^{--} and NO_3^- have similar structures, since these can be regarded as forming similar lattices with the ions Ca^{++} and Na^+. Similarity of structure of the ions is attained in the formulae given to them by Langmuir (A) or G. N. Lewis (B), in which the electrons giving the ionic charges are shown as ⊙:



Many similar cases are known. The ions O^{--} and F^- both have completed octets of the neon structure, as have Na^+ and Mg^{++}, and NaF and MgO are isomorphous. These four ions, with identical outer

electronic configurations, are called **isosteres**: a list of cases given by Langmuir of isomorphism based on isosterism is given below:

MgO ; NaF.	KCNO ; KN_3.
MgF_2 ; Na_2O.	$NaClO_3$; $CaSO_3$.
$CaCl_2$; K_2S	$KHSO_3$; $SrHPO_3$
KCl ; CaS.	$Na_2S_2O_7$; $Ca_2P_2O_7$.
$RbMnO_4$; $BaCrO_4$.	

Argon and methane resemble each other in physical properties, hence we may assume that the potassium ion, isosteric with argon but having one positive charge, will resemble the positive ammonium ion, isosteric with methane. The potassium ion (cubic) is, however, not isosteric with the ammonium ion which, like methane, has tetrahedral symmetry. In KCl crystals, the K^+ ions are each surrounded by six equidistant chlorine ions (see Fig. 214), whilst in NH_4Cl the NH_4^+ ion is surrounded by eight equidistant chlorine ions arranged like the corners of a cube about its centre (see Fig. 217*A*). Potassium and ammonium sulphates, however, are isomorphous, so that the larger volume of the sulphate ion constrains the potassium and ammonium ions into like positions.

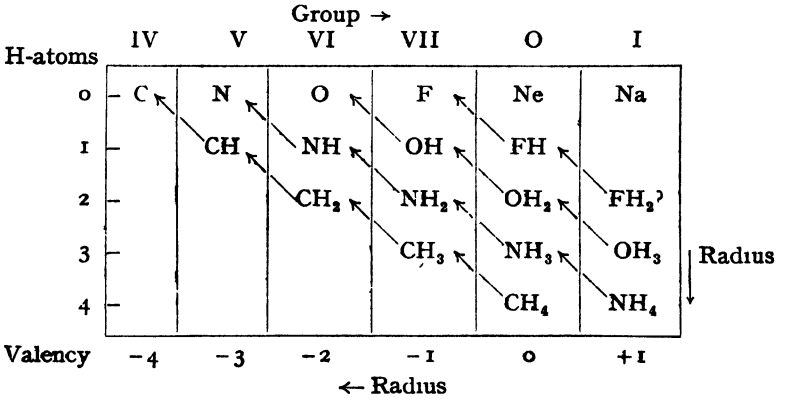
If we consider the molecules of N_2O and CO_2 as formulated by Langmuir (see Fig. 236):

$$\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} :: N :: \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \qquad \text{and} \qquad \overset{\cdot}{\underset{\cdot\cdot}{O}} :: C :: \overset{\cdot}{O},$$

we see that *each* atom has the same external configuration as neon, viz., a nucleus surrounded by an inner shell of two electrons (as in helium) and an outer shell of eight electrons. By measurement of the viscosity, the area offered by the molecules to collision may be calculated (p 224) and it is concluded that CO_2 and N_2O molecules (which have similar physical properties) behave not only as if they had the same size and shape but also as if each had practically the same outer electron configuration as that of three atoms of neon placed in line and contiguous. Again, the increase in mean diameter in each of the three groups: Ne, NH_3; A, PH_3; Kr, AsH_3, is practically the same, and in each case three hydrogen nuclei (protons) have attached themselves to an atom (N, P or As) to form the same outer electron configuration as that of the corresponding inert atom.

Information as to the outer electronic configuration of atoms and molecules has been obtained from the **Ramsauer effect**—the stopping power of the particle for slow-moving electrons. In this way $H_2(1+1)$ and He, with 2 outer electrons; Ne, A, Kr, Xe, $CH_4(4+4)$ and HCl $(1+7)$, with 8 outer electrons, behave similarly. In the examination of band spectra also, the effects due to the electrons are alike with H_2 and He; with Na, BeF, BO, CN, CO^+ and N_2^+ (all with 8 outer electrons); and with Mg, CO and N_2 (8 + 2 outer electrons).

By analogy with the Russell-Fajans-Soddy displacement law (p. 444), according to which the emission of a β-particle by the nucleus leads to an atom of the next group (At. No. increases by 1), Grimm (1925) has suggested that as the addition of a proton H^+ to the atomic kernel would lead to the same result, *e.g.*, hypothetically $O^{--} + H^+ = F^-$ (from the At. No. 8 of oxygen we arrive at At. No. 9, an isotope of fluorine), so the actual process $O^{--} + H^+ = OH^-$ should lead to a compound OH^- similar to the fluorine ion. In this way elements occupying the four places before an inert gas, by taking up 1, 2, 3 and 4 hydrogen atoms, form "pseudo-atoms" which resemble the atoms of elements in the groups 1, 2, 3 or 4 places to the right. This is illustrated by the following table. The compounds, ions or radicals in the same vertical column do, in fact, show similar properties.



CHAPTER XXVI

SULPHUR AND ITS COMPOUNDS WITH HYDROGEN AND HALOGENS

Sulphur.—From its occurrence in the free state in Sicily, sulphur, or brimstone (*brenne stone, i.e.*, combustible stone), was known to the Greeks and Romans. The use of burning sulphur in fumigation is mentioned by Homer (*c.* 900 B.C); the bleaching of textile fabrics by the fumes was carried out at an early date and sulphur was also used medicinally. The alchemists regarded sulphur as the *principle of combustibility* and a constituent of metals. 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 both free and in combination. **Free sulphur** occurs in large quantities in Italy in the volcanic regions of Sicily, and in America in the southern States of Louisiana and Texas. Less important worked deposits occur in New Zealand in Whale Island, in Chile, Russia, Iceland, and especially in Japan. More than 2,000,000 tons are now said to be produced per annum in America, or 80 per cent. of the total sulphur used in the world.

Sicilian sulphur occurs stratified with marl, clay, and rock, mostly gypsum, $CaSO_4,2H_2O$, limestone, and celestine, $SrSO_4$. It is found occasionally in large yellow transparent crystals, usually in yellow or grey crystalline masses. Fused sulphur usually deposits monclinic crystals, which on standing change into masses of very small rhombic crystals, yet rhombic crystals may be deposited on very slow cooling of large masses of molten sulphur. The sulphur in the craters of extinct volcanoes may have been formed by the interaction of volcanic gases containing hydrogen sulphide and sulphur dioxide, perhaps derived from pyrites:

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

EXPT. 1.—Invert a jar of sulphur dioxide over one of hydrogen sulphide. 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.

Since gypsum and calcium carbonate always occur in sulphur beds, the latter may be the result of the reduction of gypsum by organic matter and bacteria :

$$2CaSO_4 + 3C = 2CaCO_3 + 2S + CO_2.$$

Combined sulphur occurs in the form of metallic sulphides, many of which are important ores of metals (*i e*, serving for their extraction) · lead sulphide, *galena*, PbS, zinc sulphide, *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 Sulphur dioxide, SO_2, 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, the blackening of silver spoons by eggs is due to contained sulphur 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

The production of sulphur.—Native sulphur as dug in Sicily usually 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. 243). The ore is kindled at the top, 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.

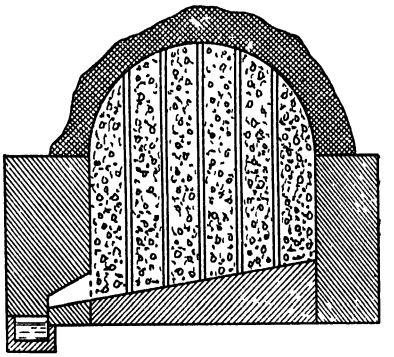


FIG. 243 —Calcaroni, or sulphur kiln.

An improved method of extraction makes use of the *Gill kiln* (1880), in which the heating is performed in closed brick chambers, with six compartments in a circle. The hot gases from one cell pass into the adjoining cell. About 75 per cent of the sulphur is recovered. Payen and Gill (1867) proposed to melt out the sulphur with superheated steam.

Sicilian sulphur is mostly *refined* at Marseilles with the apparatus shown in Fig. 244. The sulphur is fused in an iron pot, whence it flows into an iron retort heated over a fire. The sulphur boils and the vapour is conducted into a large brickwork chamber At first the vapour condenses on the cold walls as a light yellow powder, called *flowers of sulphur*. As the walls become hot, this melts (unless it is removed) and runs down as a liquid to the bottom, whence it is tapped off into cylindrical moulds to form *roll sulphur* or *brimstone*.

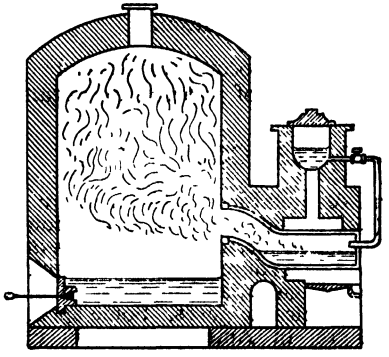


FIG 244.—Refining of sulphur by distillation

The **Frasch process of extraction**, used in America, is different. The deposit occurs below clay, quicksand and rock. A boring is made to the deposit and four concentric pipes are sunk (Fig 245). Down the two outer pipes superheated water (155°) is pumped, which fuses the sulphur. Air is then forced down the inner pipe, when an emulsion of 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.

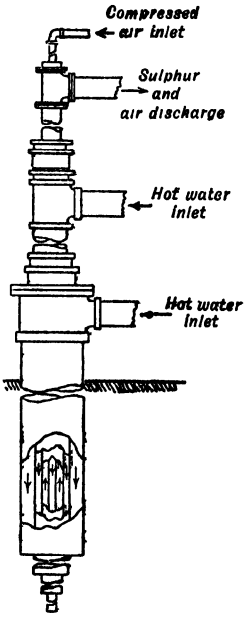


FIG. 245.—The Frasch process

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 Sulphur is formed by heating metallic sulphides at 1000° in carbon dioxide $FeS + CO_2 = FeO + CO + S$.

Sulphur from alkali-waste.—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*. Hydrogen sulphide is evolved:

(1) $CaS + CO_2 + H_2O = CaCO_3 + H_2S$, but is too largely diluted with nitrogen (present in the kiln gas) to pay for treatment. The gas is passed into a second carbonator where the hydrogen sulphide is absorbed, 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, *twice* as much hydrogen sulphide as that leaving the first vessel. It is collected in a large gas-holder over water covered with a layer of oil, is 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 hydrogen sulphide burns to sulphur dioxide, which decomposes the rest: $2H_2S + SO_2 = 2H_2O + 3S$—both SO_2 and H_2S are found in the waste gases. The recovered sulphur is very pure.

Sulphur in spent oxide.—Coal contains pyrites, FeS_2, about half the sulphur of which, during distillation in the manufacture of coal gas, comes off as hydrogen sulphide 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 burnt in a current of air to produce sulphur dioxide and this is used to make sulphuric acid.

Uses of sulphur.—**Crude sulphur** is used for making sulphur dioxide and thence sulphuric acid, for bisulphites for paper manufacture, and carbon disulphide. **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.

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 crystalline forms of sulphur.—Sulphur exists in two common crystalline forms: (1) **rhombic or α-sulphur** (Fig. 246), and (2) **monoclinic or β-sulphur** (Fig. 247). It also exists in different amorphous forms, *e.g.*, **plastic sulphur** (also called γ-sulphur, or μ-sulphur) and **colloidal sulphur.**

Rhombic or α-sulphur is prepared by allowing a solution of sulphur in carbon disulphide slowly to evaporate, when pale-yellow transparent crystals are formed, giving a lemon-yellow powder. The

density of α-sulphur is 2·06, 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 it on standing* Roll sulphur consists almost entirely of rhombic sulphur; flowers of sulphur are principally composed of it (70 per cent), but when genuine contain also a yellowish-white amorphous variety insoluble in carbon disulphide

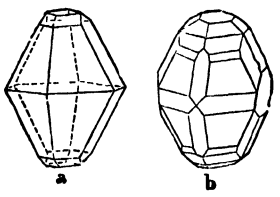


FIG 246.—Crystals of rhombic sulphur

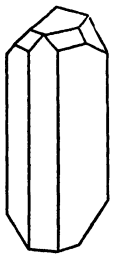


FIG 247.—Crystal of monoclinic sulphur

Monoclinic or **β-sulphur** was discovered in 1823 by Mitscherlich. Sulphur is **dimorphous** and exists in two distinct *crystalline* forms. β-sulphur is produced when fused sulphur is allowed to crystallise.

EXPT 2.—Half fill a large porcelain crucible 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. Remove the crust The inside of the crucible will be found to be lined with transparent needle-shaped crystals of β-sulphur, having usually a deeper yellow colour than α-sulphur. On standing for a few days, the crystals become opaque and brittle, and lemon-yellow. They are now aggregates of minute crystals of α-sulphur, although the original monoclinic form is preserved, the crystal is therefore called a *pseudomorph*. The transition from one form to the other is readily followed by the colour

β-Sulphur when quickly heated melts at 119·25°; it has a density of 1·96. It is insoluble in water, but soluble in carbon disulphide; the solution on evaporation deposits α-sulphur.

Crystals of β-sulphur slowly change at room temperature into minute crystals of α-sulphur, and become opaque. Crystals of α-sulphur if heated above 96° (more accurately, 95·5°), especially at 110°, slowly become opaque 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. This temperature, 96°, is called the **transition temperature** (or **transition point**) of sulphur. At the transition temperature both crystalline forms are in equilibrium, $S_\alpha \rightleftharpoons S_\beta$.

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 *monos*, one, *enantios*, opposite, *tropos*, habit).

A second distinct monoclinic variety of sulphur is deposited in pearly leaflets from a hot solution of sulphur in benzene or turpentine on rapid cooling. This form, called **nacreous sulphur** by Gernez, is monotropic.

Equilibrium between α- and β-sulphur.—α, β, liquid and vapour are different phases of sulphur and according to the Phase Rule ought to coexist under certain conditions of temperature and pressure In Fig. 248, *OP* is the vapour-pressure curve of α-sulphur; 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*, the 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) *PQ* is the vapour-pressure curve of β-sulphur, meeting *QZ* at *Q*, which defines the temperature and pressure at which S_β, liquid, and vapour are in equilibrium—it is another triple point, viz. the melting point 120° of β-sulphur under its own vapour pressure.

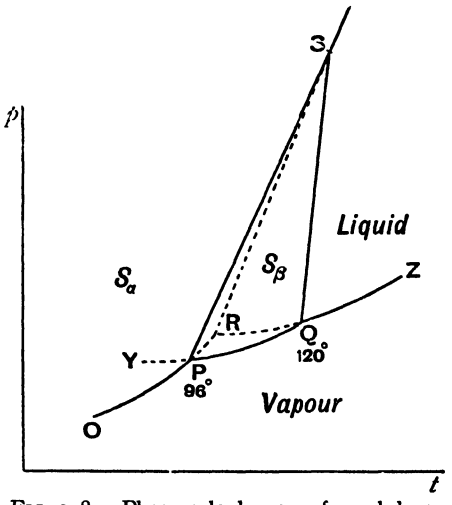


FIG. 248.—Phase rule diagram for sulphur.

PQ also crosses *OP* at *P*, the triple point at which S_α, S_β, and 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, but at different rates This is represented by two lines, starting from *P* and *Q* with different slopes

($\delta T/\delta p$), meeting ultimately at S (151°; 1288 atm.) where S_α, S_β, and liquid S are in equilibrium. Above this point S_β cannot exist, the region of its stable existence being 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 to any extent. If S_α is kept at a temperature between 96° and 112·8° for a long time, and then heated, it will not melt at 112·8° but at 120°, since it has been converted into S_β

Amorphous sulphur.—The changes which occur when sulphur is slowly heated to its boiling point are most remarkable.

EXPT 3.—When small pieces of roll sulphur are slowly and carefully heated in a test-tube, they melt at 112 8° to a clear yellow liquid. On cooling rapidly by pouring in water, S_β is produced. If the temperature is now *gradually* raised and the tube shaken, the liquid, at first quite mobile, *suddenly* becomes very viscous and its colour orange red at 180°–190°. At 230° the liquid is black and viscous. Beyond 230° the viscosity decreases but the colour remains dark, and the sulphur finally boils at 444° If the boiling sulphur is allowed to cool *slowly*, it passes through the above series of changes of colour and viscosity in the reverse order, solidifying as β-sulphur But if the boiling liquid is *quickly* cooled by being poured into cold water it forms soft rubber-like transparent threads, called **plastic sulphur**, or **γ-sulphur**.

S_γ, density 1·92, is insoluble in carbon disulphide. On standing for a few days it forms an opaque brittle lemon-yellow solid consisting partly of S_α, but some of the solid is insoluble in carbon disulphide and consists of an amorphous variety, S_μ, which forms a deep red solution in piperidine At 100° the change from viscous liquid to solid takes place more rapidly.

The plastic sulphur is obtained only if slightly impure sulphur, which has been exposed to air and contains sulphuric acid, is used. If ammonia gas is passed through the boiling sulphur, no plastic sulphur is formed on rapid cooling. In liquid sulphur, S_λ and S_μ exist in equilibrium at various temperatures · $S_\lambda \rightleftharpoons S_\mu$ the percentages of S_μ are · at 120°, 3·6; 160°, 11, 444·6°, over 30.

The rate of conversion of S_μ into S_λ on cooling is greatly increased by ammonia, which acts as a positive catalyst for the change $S_\mu \rightarrow S_\lambda$. Sulphur dioxide, sulphuric acid and traces of iodine retard the change, acting as negative catalysts and so promoting the formation of S_μ on cooling, since they stabilise this form.

EXPT. 4.—Boil 2 parts of powdered sulphur with 13 of water and 1 part of lime slaked with 3 of water, and decant the clear deep reddish-yellow liquid: $3Ca(OH)_2 + 12S = 2CaS_5 + CaS_2O_3 + 3H_2O$. Acidify the solution of calcium pentasulphide and thiosulphate (called *θεῖον ὕδωρ, thion hudor*, divine, or sulphurous, water, by Zosimos, p. 26), when a white precipitate, called **milk of sulphur** (*lac sulphuris*), is formed and hydrogen sulphide evolved (Zosimos says it is well to "hold the nose"[1]): $2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 12S$. Milk of sulphur, which is used medicinally, is soluble in carbon disulphide.

An amorphous variety called **white sulphur** remains as a pale yellow powder when genuine "flowers of sulphur" are treated with carbon disulphide, it is also formed when a solution of sulphur in carbon disulphide is exposed to sunlight, or by 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 sulphur. If a solution of sodium thiosulphate is acidified, it quickly forms a turbid colloidal suspension of sulphur. The milky liquid obtained by passing hydrogen sulphide into a solution of sulphur dioxide deposits on evaporation a gum-like mass, part of which is soluble in water (Debus, 1888). Colloidal sulphur is obtained by the interaction of 30 c.c of $3N$ sodium thiosulphate solution and 10 c c. of concentrated sulphuric acid. It is precipitated from the solution by addition of sodium chloride and centrifuging, and redissolves in water (Odén, 1913).

Two other varieties of sulphur have been described, viz., S_π and S_ϕ (or S_ρ). S_π is obtained when sulphur is heated to about 180° and rapidly cooled; the solution of the solid in CS_2 when cooled to −80° deposits S_λ, and S_π is obtained by evaporating the remaining solution in a vacuum at −80°. In solution in toluene or carbon disulphide S_π has a deep yellow colour. In solution it exists as S_4. S_ϕ is said to be produced when to concentrated hydrochloric acid at 0° a cold solution of sodium thiosulphate is added and the mixture shaken with toluene. After a short time orange-yellow crystals of S_ϕ are stated to 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. In solution it exists as S_6.

Sulphur vapour.—Sulphur boils at 444·55° and forms a deep red vapour, which when strongly heated becomes yellow. Dumas (1832) found the vapour density at 524° to be 95, corresponding with S_6; at higher temperatures the density diminishes and at 1000° Bineau (1860) found it to be 32, corresponding with S_2. Biltz (1888), working with a wider range of temperatures, found the following densities: at 468°, 113 (higher than S_7); at 524°, 102 (higher than Dumas'

figure); at 606°, 67 He concluded that at lower temperatures the molecule is S_8, but this is partially dissociated even at the boiling point: $S_8 \rightleftharpoons 4S_2$. The lowering of vapour pressure of carbon disulphide by dissolved sulphur gives the formula S_8 Bleier and Kohn (1900) found that the vapour density rises when the boiling point is lowered by diminished pressure. At 193° (2 mm. pressure), it corresponds with 7·85 atoms in the molecule. Preuner and Schupp (1909) consider that S_6 also occurs in the vapour: $S_8 \rightleftharpoons S_6 + S_2 \rightleftharpoons 4S_2$. 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

Compounds of sulphur with hydrogen.—Sulphur forms with hydrogen a gaseous compound H_2S, **hydrogen sulphide** (or *sulphuretted hydrogen*, as it is sometimes called) 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, $(H_2O)_n$. At least two liquid **hydrogen persulphides**, H_2S_2, and H_2S_3, are known.

Hydrogen Sulphide.—When hydrogen is passed over boiling sulphur in a bulb-tube, the issuing gas contains a small amount (1 or 2 per cent) of hydrogen sulphide and blackens lead acetate paper owing to the formation of lead sulphide, PbS. If pure hydrogen sulphide is heated, partial decomposition occurs with deposition of sulphur. The reaction is reversible: $H_2 + S \rightleftharpoons H_2S$. The pure gas is best prepared synthetically in presence of pumice as a catalyst at 600°, when the reaction is practically complete. If a stream of powerful sparks is passed through H_2S, sulphur is deposited and nearly pure hydrogen remains.

Traces of hydrogen sulphide are formed when sulphur is boiled with water $4H_2O + 4S \rightleftharpoons 3H_2S + H_2SO_4$ The gas is formed when heavy naphtha (sp gr. 0 9) is dropped into boiling sulphur in a flask, and it is evolved in a regular stream on heating a mixture of powdered sulphur, paraffin wax, and ignited asbestos Hydrogen in the hydrocarbons is substituted by sulphur (S replaces 2H).

Hydrogen sulphide is usually prepared by the action of dilute sulphuric acid, or better, hydrochloric acid (1 : 3) on ferrous sulphide: $FeS + 2HCl = FeCl_2 + H_2S$. The reaction is carried out in a Kipp's apparatus so that the supply of the gas, which has a most unpleasant

odour and is poisonous, may be interrupted at will. It is washed with a little water before use. On account of the presence of free iron in the ferrous sulphide the gas contains hydrogen, which does not interfere with its use in qualitative analysis

Hydrogen sulphide free from hydrogen is obtained by heating powdered antimony sulphide (*stibnite*) with concentrated hydrochloric acid. $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$. The pure gas is obtained by treating calcium sulphide with hydrochloric acid: $CaS + 2HCl = CaCl_2 + H_2S$, or by heating to 60° a solution of magnesium hydrosulphide obtained by passing the impure gas through magnesia suspended in water:

$$MgO + 2H_2S \rightleftharpoons Mg(HS)_2 + H_2O.$$

When a mixture of 2 vols of concentrated sulphuric acid and 1 vol. of water is heated with zinc, hydrogen sulphide is formed:

$$4Zn + 5H_2SO_4 = 4ZnSO_4 + 4H_2O + H_2S.$$

A little sulphur is deposited The concentrated acid gives only sulphur dioxide: $Zn + 2H_2SO_4 = ZnSO_4 + SO_2 + 2H_2O$.

The action of acids on sulphides.—Ferrous sulphide is very slightly soluble in water, and is almost wholly ionised at great dilution: (1) $FeS \rightleftharpoons Fe^{\cdot\cdot} + S''$ The solubilities of some sparingly soluble precipitated sulphides are given below, in gm. per litre at 18°:

MnS	$6{\cdot}09 \times 10^{-3}$	CdS	$1{\cdot}3 \times 10^{-3}$	CuS	$3{\cdot}36 \times 10^{-4}$
FeS	$6{\cdot}17 \times 10^{-3}$	PbS	$8{\cdot}6 \times 10^{-4}$	HgS	$1{\cdot}25 \times 10^{-5}$
ZnS	$6{\cdot}9 \times 10^{-3}$	Bi_2S_3	$1{\cdot}8 \times 10^{-4}$	Ag_2S	$1{\cdot}37 \times 10^{-6}$

Hydrogen sulphide is a weak dibasic acid: (2) $H_2S \rightleftharpoons H^{\cdot} + HS' \rightleftharpoons 2H^{\cdot} + S''$; the second stage of ionisation is very slight. The concentration of S'' formed in (2) is therefore still less than that formed in consequence of (1) On adding a strong acid the H 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 mass-action 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 $[H^{\cdot}]$ 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 hydrogen sulphide accumulating stops the reaction before solution is complete, and strong acid must be used, or the hydrogen sulphide must be removed from the liquid by boiling or by a current of air.

Properties of hydrogen sulphide.—The gas may be collected over hot water; it is appreciably soluble in cold water (4·37 vols. at 0°, 3·40 vols. at 10°, 2·6 vols. at 20°; 1 vol. of alcohol at 15° dissolves 9·54 vols. of H_2S). It may be collected by displacement, since its density is 1·2 (air = 1). It attacks mercury slowly, unless it is dry and free from oxygen For ordinary purposes it may be dried by calcium chloride, but if required pure it should be dried with *purified* phosphorus pentoxide, or by liquefaction and fractionation.

Hydrogen sulphide is a colourless gas with a powerful odour of rotten eggs (decaying albumin evolves H_2S), and is poisonous; it liquefies at −60·7°, the vapour pressure at 12° being 15 atm. At lower temperatures it forms a transparent solid, melting at −85·6°. The critical temperature is 100·4°, the critical pressure 89·05 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 1 c.c. of glycerin to 50 c.c. of saturated solution. In decinormal solution 0·095 per cent. is ionised to $H' + HS'$; the further stage to S'' is very slight:

$$[H'][HS']/[H_2S] = 9·1 \times 10^{-8},$$
$$[H'][S'']/[HS'] = 1·2 \times 10^{-15}.$$

A solid crystalline hydrate with $5H_2O$ or $6H_2O$ is formed at low temperatures.

The gas is decomposed by electric sparks, by a heated platinum spiral: $H_2S \rightleftharpoons H_2 + S$, and by heated tin or lead, giving its own volume of hydrogen and solid sulphur or sulphides of the metals: $H_2S + Sn = H_2 + SnS$. Its density is 17, hence the molecular weight is 34. Of this the hydrogen, one molecule per molecule of gas, accounts for 2, and hence the sulphur is $34 - 2 = 32$, which is the atomic weight; hence the formula is H_2S.

Chlorine decomposes hydrogen sulphide and sulphur is deposited: $H_2S + Cl_2 = 2HCl + S$, but sulphur chloride is usually also formed. A solution of hydrogen sulphide, treated with a large excess of chlorine water, yields 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 in aqueous or alcoholic solution. Hydrogen sulphide may be determined by titration with iodine solution. The solution must not contain more than 0·04 per cent. of H_2S:

$$H_2S + I_2 = 2HI + S.$$

The gas ignites in air at 364° and burns in air or oxygen with a blue flame; owing to the high temperature it is completely dissociated in the interior of the flame, and 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: $2H_2S + O_2 = 2H_2O + 2S$. 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 oxygen explodes violently on ignition

The gas or its solution (*e g.*, in 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, not produced by free H_2S, with a freshly-prepared solution of sodium nitroprusside. The gas decomposes concentrated sulphuric acid: $H_2SO_4 + H_2S = S + SO_2 + 2H_2O$. It is absorbed by caustic alkalies, forming sulphides.

$$NaOH + H_2S = NaHS + H_2O,$$
$$2NaOH + H_2S = Na_2S + 2H_2O$$

Fuming nitric acid reacts violently with the gas, ignition and perhaps explosion occurring. Very dilute (5 per cent.) nitric acid is not affected; with more concentrated acid (43 per cent) the products are sulphuric acid, sulphur, ammonia, nitrous acid, nitric oxide and nitrous oxide A solution containing 23 per cent. of nitric acid and 15 per cent. of sulphuric acid is inert towards the gas, whether prepared by mixing or by the reaction itself.

Precipitation of metallic sulphides.—Hydrogen sulphide precipitates sulphides from solutions of salts of many metals. These sulphides often have characteristic colours, and hydrogen sulphide is used as a reagent in qualitative analysis.

EXPT. 5.—Pass a current of hydrogen sulphide through a series of wash-bottles 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 (bismuth, brownish black), CuS, PbS, HgS, Bi_2S_3; cadmium, tin (stannic) and arsenic give *yellow* sulphides, CdS, SnS_2, 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. 6.—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. Zinc sulphide,

ZnS, is white; manganous sulphide, MnS, is flesh-coloured (sometimes greenish); nickel, cobalt and iron give black NiS, CoS and FeS

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 $1{\cdot}3N$ 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.

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

In $2N$ $(NH_4)_2S$ solution, $[S''] = 3 \times 10^{-10}$; $[H^{\cdot}] = 5 \times 10^{-10}$ (Knox). (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 hydrogen sulphide ($CaS + H_2S \rightleftharpoons Ca(SH)_2$) (v) Aluminium and chromium salts give precipitates of *hydroxides* with ammonium sulphide, since their sulphides are completely hydrolysed by water:

$$2Al''' + 3S'' + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

The precipitation of sulphides is complicated by the occurrence of modifications with different solubilities Cobalt and nickel sulphides are not precipitated by hydrogen sulphide from acid solutions, but when the precipitates have been formed by ammonium sulphide in alkaline solution they are insoluble in dilute acids Two modifications of zinc sulphide are precipitated, one (α-ZnS) in acid solution and another (β-ZnS) in alkaline solution, the second form having five times the solubility of the first. In acid solutions the precipitation of zinc sulphide shows a period of induction, which is longer the more acid is the solution. In some cases no precipitate is formed, although zinc sulphide is almost insoluble in the strength of acid used. Other sulphides, *e g.* CuS and CdS, however, bring about simultaneous precipitation of the zinc sulphide.

Hydrogen persulphides.—If an acid is added to the yellow solution of polysulphides of calcium (p. 491), which contains CaS_2 and probably CaS_5, hydrogen sulphide 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 (1831) regarded as **hydrogen persulphide**, H_2S_2, analogous to H_2O_2:

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

EXPT. 7.—To 250 cc of a cooled mixture of equal volumes of concentrated HCl and water in a beaker add in a thin stream, with vigorous stirring, 100 cc of *thion hudor* (p. 491). Insert a piece of litmus paper into the milky liquid and notice that it is bleached. Pour the liquid into a separating funnel. After a few hours a yellow oil, heavier than water, separates.

The oil has a pungent smell, its sp gr is 1·7; it is soluble in benzene and carbon disulphide, but is sparingly soluble in and decomposed by alcohol It slowly decomposes spontaneously, especially on warming, into hydrogen sulphide 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 composition of the oil 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 probably 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 had a composition intermediate between H_2S_2 and H_2S_3 Sabatier concluded that it was H_2S_2 + dissolved sulphur. Bloch and Hohn (1908) by using glass vessels treated with hydrochloric acid to remove alkali (which decomposes the persulphide), separated the crude oil dried by calcium chloride which had been treated with hydrogen chloride gas, by distillation in small portions 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° to – 53° collected, 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

$$S\,S\!\begin{matrix}H\\H\end{matrix} \rightleftharpoons HS{\cdot}SH;\quad S\,S\,S\!\begin{matrix}H\\H\end{matrix} \rightleftharpoons S.SH{\cdot}SH \rightleftharpoons HS{\cdot}S{\cdot}SH$$

Hydrogen pentasulphide, H_2S_5, is formed (Mills and Robinson, 1928) as a clear yellow oil (which decomposes on distillation) by the reaction between ammonium pentasulphide crystals and anhydrous formic acid:

$$(NH_4)_2S_5 + 2H{\cdot}COOH = 2H{\cdot}COONH_4 + H_2S_5.$$

The ammonium pentasulphide separates in yellow crystals from the deep red solution formed by passing hydrogen sulphide, in absence of air, into 40 gm. of powdered sulphur suspended in 100 c c. of ammonia solution (sp. gr. 0·88)

Halogen compounds of sulphur.—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 sulphur may be surrounded by a shell of 12 shared electrons, not 8 as in many other compounds. 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 −50·8°. 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.

A **monofluoride**, S_2F_2, is obtained as a colourless gas, b. pt −99°, m. pt. −105·5°, by heating silver fluoride with sulphur $2AgF + 3S = Ag_2S + S_2F_2$. A gaseous **tetrafluoride**, SF_4, b pt −40°, m pt. −124°, is formed by heating sulphur with cobaltic fluoride: $4CoF_3 + S = 4CoF_2 + SF_4$. It is decomposed by water.

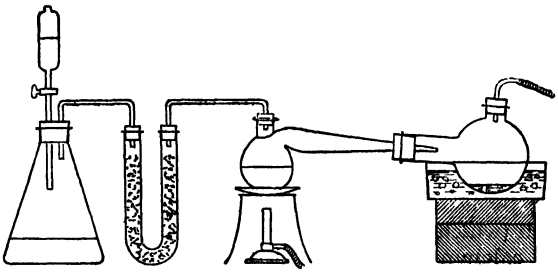


FIG. 249.—Preparation of sulphur monochloride.

Sulphur monochloride, S_2Cl_2, is prepared by passing dry chlorine over sulphur fused in a retort (Thomson, 1804). A red liquid distils over into a cooled receiver (Fig. 249). By rectification of this over powdered sulphur, a clear amber-coloured liquid, sp gr. 1·706, boiling at 138°, is obtained, which solidifies at −80°. Sulphur monochloride has a vapour density of 67·6, which corresponds with S_2Cl_2 ($\Delta = 67·0$), but the liquid dissociates slightly on boiling. It 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 hydrolysis:

$$S_2Cl_2 + 2H_2O = 2HCl + H_2S + SO_2;$$
$$2H_2S + SO_2 = 2H_2O + 3S.$$

The liquid is only slowly decomposed by water; hydrochloric acid and sulphur are formed, together with various oxy-acids of sulphur (*e.g.*, pentathionic acid). Metals decompose it on heating, forming chlorides and sulphides. Sulphur chloride dissolves sulphur readily (66 per cent.). It also dissolves iodine, many halide salts of metals, and organic compounds. The salt solutions are poor conductors, and on account of its small dielectric constant (4·9) the liquid has only a slight ionising power. The formula may be S : S : (Cl_2).

If the monochloride is saturated with chlorine at room temperature, a ruby red liquid containing SCl_2, the **dichloride**, is formed, but this decomposes on distillation. At $-22°$, the action of chlorine on the monochloride produces a **tetrachloride**, SCl_4. This freezes to a yellowish-white solid, melting at $-30°$ On taking the liquid out of the freezing mixture, it decomposes. Stable crystalline double compounds, *e g*, $SbCl_5$,SCl_4, are known Lowry, McHatton and Jones (1927) found that samples of chlorinated sulphur chloride after heating in a sealed tube at 100°, gave freezing-point curves exhibiting not only maxima corresponding with S_2Cl_2 and SCl_4, but also breaks which are attributed to the crystallisation of SCl_2 and a new chloride, S_3Cl_4 Although an equilibrium mixture having the composition SCl_2 deposits SCl_4 on freezing, freshly prepared mixtures of S_2Cl_2 with an over-chlorinated sample of sulphur dichloride gave a temporary maximum freezing-point corresponding with SCl_2: $SCl_4 + S_2Cl_2 = 3SCl_2$, followed on standing by $2SCl_2 = S_2Cl_2 + Cl_2$. Solid SCl_2 can be frozen out of the fresh mixture and crystallised from light petroleum by cooling in liquid air. **Sulphur monobromide**, S_2Br_2, is a garnet-red liquid, b pt 57°/0·22 mm., m. pt. $-46°$, obtained by heating sulphur with bromine in a sealed tube. No iodide is known.

CHAPTER XXVII

THE OXYGEN COMPOUNDS OF SULPHUR

Oxygen compounds of sulphur.—The following oxides and oxy-acids of sulphur are known.

Sulphur monoxide, SO, is a gas formed by the action of an electric discharge on a mixture of sulphur dioxide and sulphur vapour at 10 mm pressure it is stable at room temperature but decomposes at 100° $2SO = S + SO_2$ (Cordes and Schenk, 1933)

Sulphur sesquioxide, S_2O_3. corresponding with **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 **perdisulphuric acid**, $H_2S_2O_8$

Sulphur tetroxide, SO_4(?), the anhydride of **permonosulphuric acid**, H_2SO_5

Hyposulphurous acid,	$H_2S_2O_4$		
Sulphurous acid,	H_2SO_3	**Dithionic acid,**	$H_2S_2O_6$
Sulphuric acid,	H_2SO_4	**Trithionic acid,**	$H_2S_3O_6$
Thiosulphuric acid,	$H_2S_2O_3$	**Tetrathionic acid,**	$H_2S_4O_6$
Pyrosulphuric acid,	$H_2S_2O_7$	**Pentathionic acid,**	$H_2S_5O_6$
Perdisulphuric acid,	$H_2S_2O_8$	**Hexathionic acid,**	$H_2S_6O_6$
Permonosulphuric acid,	H_2SO_5		

Sulphur Dioxide

Sulphur dioxide.—Homer refers to the use of burning sulphur in fumigation, and Pliny states that the fumes were 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), his followers 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; it is sulphur dioxide, SO_2

The combustion of sulphur.—When 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 363° 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, 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 (Tyndall ; Morren, 1870).

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.*

EXPT. 1.—A small piece of sulphur in a metal spoon is kindled in dry oxygen over *dry* mercury in the apparatus shown in Fig. 250, by means of a piece of fine platinum wire heated electrically in contact with the sulphur. When the apparatus is cool, the mercury levels are practically unchanged.

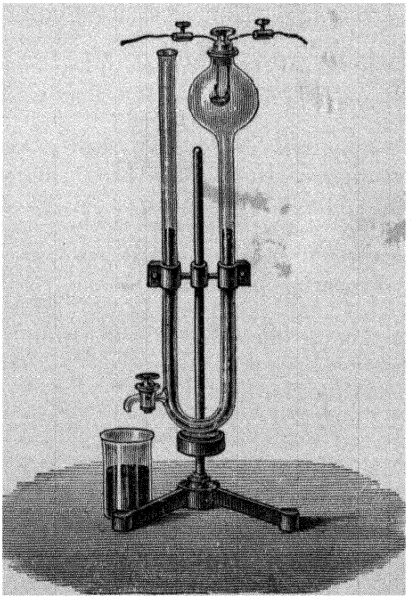


FIG. 250.—Volumetric composition of sulphur dioxide.

The (approximate) relative density of sulphur dioxide is 32. The approximate molecular weight is therefore 64. The above experiment shows that the molecular weight of the gas contains a molecular weight of oxygen, $O_2 = 32$, hence the remainder, $64 - 32 = 32$, is the weight of sulphur. But this is the atomic weight, hence the formula is SO_2.

A mixture of sulphur dioxide with nitrogen is prepared on the large scale by the combustion of sulphur or of iron pyrites in a current of air in special burners :

$$S + O_2 = SO_2 ;$$
$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

Sulphur dioxide is used in bleaching wool and straw, as a disinfectant, very largely in making sulphites for the paper industry, and in the manufacture of sulphuric acid.

Preparation of sulphur dioxide.—In the laboratory sulphur dioxide gas is usually made by the reduction of sulphuric acid. If the concentrated acid is heated with copper, mercury, silver, sulphur, or charcoal, sulphur dioxide is formed :

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O ;$$
$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O ;$$
$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O ;$$
$$S + 2H_2SO_4 = 3SO_2 + 2H_2O ;$$
$$C + 2H_2SO_4 = 2SO_2 + CO_2 + 2H_2O$$

EXPT. 2 —Copper turnings are covered with concentrated sulphuric acid in a flask fitted with a thistle funnel, and heated on wire gauze The mixture becomes dark and gas is evolved with effervescence. When this occurs the flame is lowered or removed. The gas is collected by downward displacement, or over mercury. It may be dried by concentrated sulphuric acid 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.

A convenient method of preparation is to drop concentrated sulphuric acid into a saturated solution of sodium hydrogen sulphite (" bisulphite ") :

$$2NaHSO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2SO_2$$

Properties of sulphur dioxide.—Sulphur dioxide is a colourless gas, 2·264 times heavier than air (normal density = 2·9267 gm /lit.), with a choking smell well known as that of burning sulphur, and is poisonous. It does not support combustion in the ordinary sense, but heated potassium burns in it :

$$4K + 3SO_2 = K_2SO_3 \text{ (sulphite)} + K_2S_2O_3 \text{ (thiosulphate)}.$$

Finely-divided tin and iron also burn in the gas when heated, 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 2·5 atm pressure at 15°, SO_2 forms a colourless liquid, b. pt. −10·0° ; on rapid evaporation this freezes to a snow-like solid, m. pt. −72·7°. The critical temperature is 157·15°, the critical pressure 77·65 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, so that the solvent has ionising properties. Its dielectric constant is 13·75.

Expt. 3.—The liquid is easily prepared by passing the gas through a glass spiral immersed in a mixture of pounded ice and salt (Fig. 251); it 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.

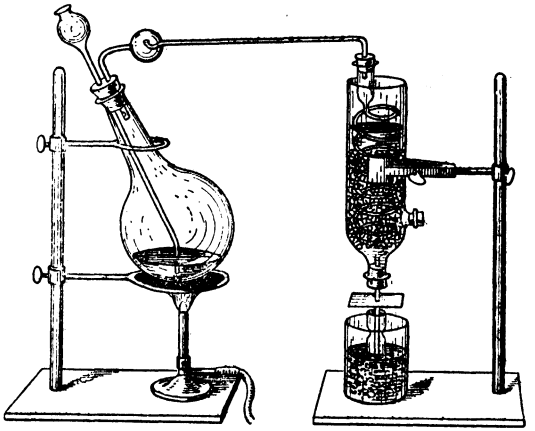


Fig. 251.—Liquefaction of SO_2 by cooling.

Sulphurous acid.—Sulphur dioxide is freely soluble in water, 45 vols. to 1 of water at 15°, forming a liquid smelling strongly of the gas and acid to litmus. One vol. of glacial acetic acid absorbs 318 vols. of sulphur dioxide at 15°. The aqueous solution probably contains the unstable sulphurous acid, H_2SO_3, but the latter has never been isolated. On boiling, all the 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: hyposulphurous acid is formed as an intermediate product, but the final result is: $3H_2SO_3 = 2H_2SO_4 + H_2O + S$ (*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 Pliny, 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. 4.—Add a solution of sulphur dioxide to a dilute fuchsine ("magenta") solution: the red colour is discharged. On boiling the colour is restored.

Expt. 5.—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 acid 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: $I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$. The solution of SO_2 readily absorbs atmospheric oxygen; the rate of oxidation is greatly reduced by the addition of glycerin, phenol, mannitol, benzaldehyde, or (especially) stannous chloride.

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 in 10^{12} litres exerts an appreciable influence. Organic substances may form complex compounds with the metal ions, their action as negative catalysts may therefore consist in their capability of destroying the positive catalysts ($Cu^{\cdot\cdot}$, etc.). Another explanation is that negative catalysts break the "chains" of molecules produced by activation in a reaction (p. 200), and a further theory is that the negative catalyst (inhibitor) combines with one of the reacting substances.

Sulphurous acid solution evolves hydrogen with magnesium. Sulphur dioxide and sulphites are reduced to hydrogen sulphide by zinc and hydrochloric acid; they precipitate SnS_2 from a solution of stannous chloride in hydrochloric acid.

Sulphur dioxide decolorises a solution of potassium permanganate:

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

A piece of paper dipped in acidified potassium dichromate solution (yellow) becomes green in sulphur dioxide:

$$2CrO_3 + 3SO_2 = Cr_2(SO_4)_3.$$

Sulphites.—Sulphurous acid is diabasic and forms two series of salts, which theoretically would have the formulae $MHSO_3$ and M_2SO_3.

EXPT. 3.—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 the reaction:

$$2HSO_3' = S_2O_5'' + H_2O \rightleftharpoons 2SO_3'' + 2H^{\cdot}.$$

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 :

$$SO_3'' + H_2O + Cl_2 = SO_4'' + 2Cl' + 2H^{\cdot}.$$

If a solution of sodium hydrogen sulphite is evaporated with excess of sulphur dioxide, or if sulphur dioxide is passed over crystals of sodium carbonate, Na_2CO_3,H_2O, the salt $Na_2S_2O_5$, **sodium metabisulphite** (*i.e.*, $Na_2O,2SO_2$), used in photography, is formed On heating dry sodium sulphite, the sulphate and sulphide are formed :

$$4Na_2SO_3 = Na_2S + 3Na_2SO_4.$$

The metabisulphite on heating first produces Na_2SO_3, and SO_2, and the Na_2SO_3 then decomposes as above The simple acid sulphites, *e g*, $NaHSO_3$, do not appear to exist

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 bivalent *thionyl* radical, —SO—, is a colourless liquid, sp. gr. 1·677 at 0°, which 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 :

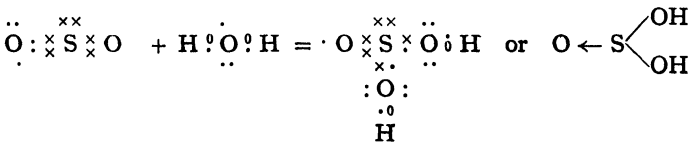
$$SO\begin{matrix}Cl\\Cl\end{matrix} + \begin{matrix}HOH\\HOH\end{matrix} = SO\begin{matrix}OH\\OH\end{matrix} + \begin{matrix}HCl\\HCl\end{matrix} \rightleftharpoons SO_2 + H_2O + 2HCl.$$

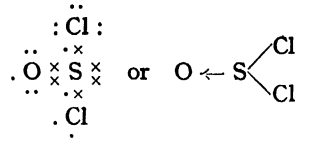
Thionyl bromide, $SOBr_2$, is a red liquid, b pt 59°/40 mm., formed by acting on $SOCl_2$ with gaseous HBr. Thionyl chlorobromide, SOClBr, was said by Besson also to be produced in this reaction, but Mayes and Partington (1926) were unable to find any trace of it. **Thionyl fluoride**, SOF_2, is a colourless 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 HO.SO OH. By the action of thionyl chloride on alcohol **symmetrical diethyl sulphite**, EtO.SO OEt, b. pt. 161°, is formed.

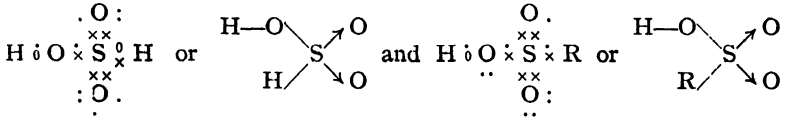
By the oxidation of **mercaptan**, EtSH, with dilute nitric acid, **ethyl-sulphonic acid**, $EtSO_3H$, is formed, the ethyl ester of which, $EtSO_3Et$, is obtained by the action of sodium sulphite on ethyl iodide. In the sulphonic acid the ethyl group is directly attached to sulphur, as in mercaptan. Sulphurous acid, therefore, appears to possess two formulae, the symmetrical HO SO.OH, and the unsymmetrical, $H.SO_2.OH$ (sulphonic acid).

The electronic formula of sulphur dioxide may be written as , *i.e.*, O=S→O, and the formation of sulphurous acid as :

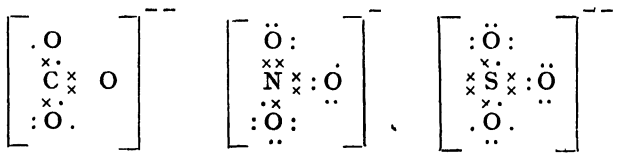


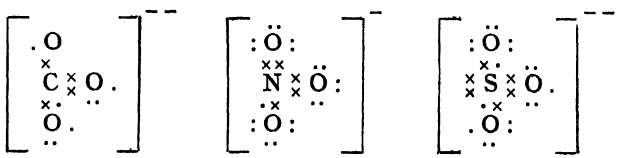
and thus thionyl chloride is 

The unsymmetrical formula for sulphurous acid, and that for a sulphonic acid (R = Et, etc) may be written .



The sulphite ion is probably triangular in structure The carbonate, nitrate and sulphite ions are very similar in structure, and many sulphites and carbonates are isomorphous



or 

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 or chromium, vanadium pentoxide or silver vanadate heated to 600°–700° (Wohler): $2SO_2 + O_2 \rightleftharpoons 2SO_3$. A state of equilibrium is set up, since the reaction is reversible:

$$[SO_3]^2/[SO_2]^2 \times [O_2] = K$$

Excess of oxygen favours the production of the trioxide.

At 450°, 2 per cent. of pure SO_3 is decomposed, at 700°, 40 per cent. In a mixture of SO_2 and air such as is obtained by burning pyrites, 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°, 99, at 550°, 85; at 645°, 60. The reverse change, $2SO_3 = 2SO_2 + O_2$, is favoured by rise of temperature since it absorbs heat (p. 316). The direct change.

$$2SO_2 + O_2 = 2SO_3 + 45 \text{ k. cal.}$$

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. 7.—Pass SO_2 and O_2 through sulphuric acid in a Woulfe's bottle to dry them and then over dry platinised asbestos heated in a hard glass tube. Sulphur trioxide is produced, which condenses (although not readily) in a strongly-cooled dry receiver to a colourless liquid, which gradually solidifies.

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 on the small scale by distilling **fuming sulphuric acid** in a retort and collecting the trioxide in a perfectly dry receiver cooled in a freezing mixture: $H_2S_2O_7 \rightleftharpoons H_2SO_4 + SO_3$. In this way it was first obtained by Bernhardt in 1755. If sodium hydrogen sulphate is heated at 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 calcined ferrous sulphate was described by "Basil Valentine": this may have been sulphur trioxide: $2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$.

Sulphur trioxide exists in more than one modification. The liquid, b. pt 44·52°, at first obtained, solidifies on cooling to transparent crystals melting at 16·8°, sp. gr. 1·9255 at 20°. This form is called α-SO_3. If α-SO_3 is allowed to stand some time, at least in presence of a trace of moisture, it forms silky asbestos-like crystals of β-SO_3, and there may be two forms of this. At 50°, the β-form changes slowly into the α-form

The vapour density of sulphur trioxide corresponds with the formula SO_3 When passed through a red-hot tube the vapour is decomposed, giving 2 vols of SO_2 and 1 vol. of O_2 which do not recombine on cooling in the absence 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 $\cdot H_2O + SO_3 = H_2SO_4$ It dissolves in water with a loud hissing noise and considerable evolution of heat, but dissolves readily and quietly 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 by the contact process.—When platinum is used technically as a catalyst the gases must be carefully purified, since otherwise the platinum loses its activity, or is "poisoned" (p 164). Arsenious oxide, sulphuric acid fog, and dust in the gases from pyrites burners, are removed by introducing steam and cooling, then filtering the gas through coke wetted with concentrated sulphuric acid until no fog is seen by a powerful beam of light ("optically clear" gas). In modern plants, platinum has been replaced by a preparation of vanadium pentoxide as the catalyst.

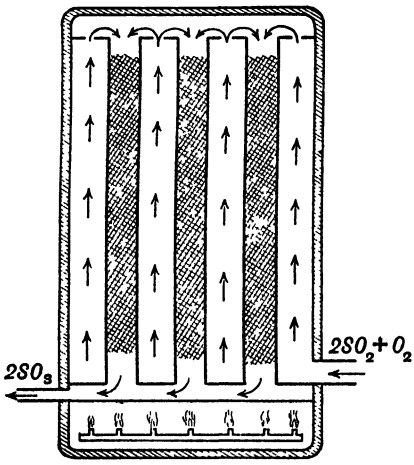


FIG 253.—Badische converter.

In the **Badische process** the purified gas is passed through an iron converter (Fig. 253), with 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 gas burners to start the reaction. By letting the incoming gas sweep over the outside of the hot tubes in which reaction occurs, no external heating is needed, since a considerable amount of heat is evolved, and the process goes on continuously at 400°–450°.

In the **Schröder-Grillo process**, 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 contact mass, on which the platinum is very finely divided. This is put on shelves in iron converters, lagged outside (Fig 254), and when the process is started it goes on without external heating

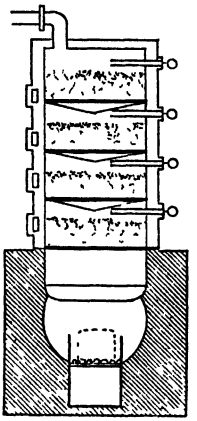


FIG 254 —Schröder-Grillo converter

The **Mannheim process** utilises burnt pyrites (Fe_2O_3 and a little CuO) as the contact mass This is filled into a rectangular tower, the lower part of which communicates with four pyrites burners arranged in a +, to which air dried in a sulphuric acid tower is supplied (Fig. 255) 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

The **Tenteleff process** utilises a catalyst composed of asbestos "sponge-cloths" soaked in platinic chloride and the latter reduced by formaldehyde These are superposed in an iron frame, 3 ft. by 2 ft, interposed in the gas current The temperature is 450°–500°.

The sulphur trioxide cannot be absorbed from the converter gas 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

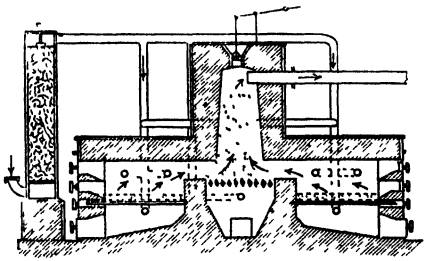


FIG 255 —Mannheim contact process

Fuming sulphuric acid 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. 10·49°); H_2SO_4,H_2O or $SO_3,2H_2O$ (m pt 8·62°); $H_2O,2SO_3$ or $H_2S_2O_7$ (**pyrosulphuric acid**, m. pt 35°); $H_2SO_4,2H_2O$, m. pt. −38·9°, and $H_2SO_4,4H_2O$ (m. pt. −29°) 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 may be added to ordinary acid to increase its concentration.

Sulphuric acid.—Moistened flowers of sulphur when exposed to air are slowly oxidised to sulphuric acid. Sulphurous acid 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: $SO_2 + H_2O_2 = H_2SO_4$, or when chlorine water, bromine water, or nitrous acid is added:

$$H_2SO_3 + H_2O + Cl_2 = H_2SO_4 + 2HCl;$$
$$SO_2 + 2HNO_2 = H_2SO_4 + 2NO.$$

Sulphuric acid or *oil of vitriol* is mentioned by the mediaeval alchemists, who obtained it by distilling *green vitriol*, *i.e.*, ferrous sulphate $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. In 1666 Le Fèvre obtained the acid by burning sulphur in presence of moisture, Lemery in 1675 made it 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 at Prestonpans replaced the fragile glass vessels by lead chambers 6 ft wide, and these were enlarged in later works These chambers were introduced into France in 1766 by the Englishman Holker, and in 1774 La Follie 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 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 in 1827 and 1859, respectively, led to the modern industry. The chamber process has been considerably improved and is still very largely used for making ordinary (not fuming) sulphuric acid

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"). Clement and Desormes discovered an intermediate compound in the reaction, viz., **nitrososulphuric acid** ("chamber crystals"), *i.e.* sulphuric acid $HO \cdot SO_2 \cdot OH$, in which H is replaced by the nitroso-group

NO. It may be formed and decomposed alternately in the chambers:

(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 gas N_2O_3, really a mixture $NO_2 + NO$, therefore acts in a cyclic manner, *i e*, as a catalyst.

EXPT. 8.—A dry 6-litre flask, *A*, is fitted with four inlet tubes as shown in Fig 256, 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, the third to a gas-holder containing nitric oxide and the fourth 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 red gaseous 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 nitroso-sulphuric acid form on the inside of the globe. The colour of the gases becomes paler. Sweep out the gases by a rapid current of dry oxygen, and boil the water in *B*. When the steam comes in contact with the crystals they dissolve with effervescence, producing red oxides of nitrogen. The liquid in the flask gives a white precipitate ($BaSO_4$) with $BaCl_2$ solution. (If insufficient water vapour is used in the first stage, a white powdery deposit is formed which gives purple droplets in contact with steam.)

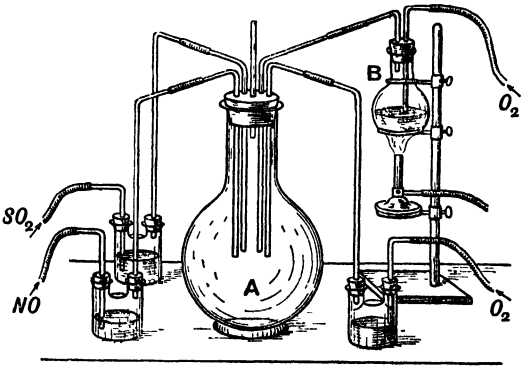


FIG 256.—Experiment illustrating reactions in sulphuric acid chambers

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 ashpits. 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," 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. Sulphur is burnt in large inclined rotating cylinders or other type of special burner.

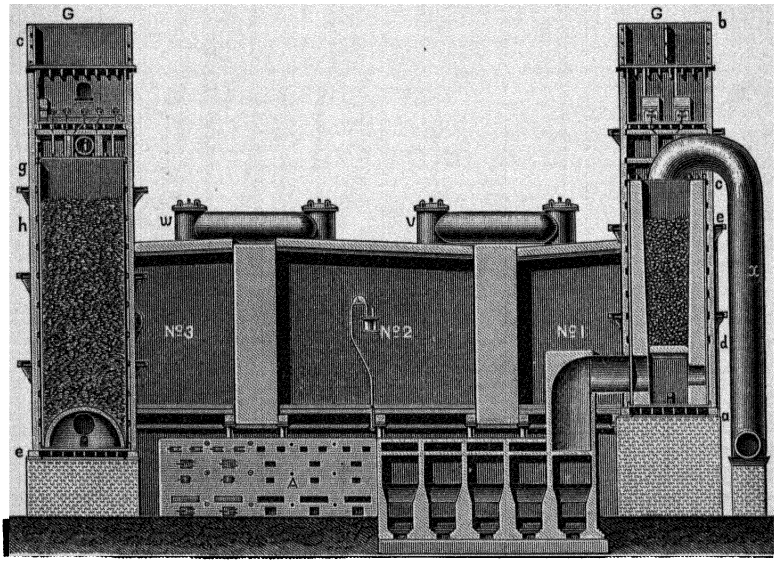


FIG. 257.—Diagram of sulphuric acid chamber plant, showing end view of three chambers, Gay-Lussac tower (left), Glover tower (right) and pyrites burners, *A*.

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 sulphur burnt as pyrites are required. In modern plants, the oxides of nitrogen are supplied by the oxidation of ammonia.

From the nitre-oven the gases pass, at 300°–400°, into the **Glover tower** seen on the right in Fig. 257, 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 pass two streams of acid from

tanks at the top, one of acid (65–70 per cent. H_2SO_4) from the lead chambers, the other 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 chamber 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 part of the steam for the chambers. About 25 per cent of the total acid made is formed by reactions in the Glover tower

From the Glover tower the gases pass by a lead main seen on the extreme right of Fig 257, to the first of the set of **lead chambers**, the ends of three of which are shown These are of sheet lead weighing 6–8 lb per sq ft , are oblong or square in shape and dip into large lead trays 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 Drum-shaped or polygonal chambers, sometimes cooled by water flowing over the outside, or even packed towers, are used in some modern plants

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 or less is allowed per lb. of sulphur 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. 257, 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. of 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. In modern practice a high concentration of oxides of nitrogen (" circulating nitre ") with adequate absorption capacity in the Gay-Lussac towers is used, and the reaction proceeds rapidly.

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 :

$$(1)\ NO_2 + SO_2 + H_2O = H_2SO_4 + NO$$
$$(2)\ 2NO + O_2 = 2NO_2.$$

Davy put forward another explanation, elaborated by Lunge. According to this, nitrososulphuric acid, $SO_2(OH)\cdot O\cdot NO$, is an intermediate product formed by the action of nitrous anhydride, N_2O_3, traces of which exist in equilibrium with NO and NO_2

$$(1)\ 2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH)\cdot O\cdot NO.$$

It 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 reaction may occur .

$$2SO_2(OH)\cdot O\cdot NO + SO_2 + 2H_2O = 3SO_2(OH)_2 + 2NO$$

In a more recent theory Lunge (1906) assumed the formation of **nitrosisulphonic acid**, H_2SNO_5, which then forms nitrososulphuric acid, $HSNO_5$, the latter being decomposed as described above.

$$SO_2 + NO_2 + H_2O = H_2SNO_5$$
$$2H_2SNO_5 + O = H_2O + 2HSNO_5$$
$$2H_2SNO_5 + NO_2 = 2HSNO_5 + NO + H_2O$$

Raschig (1887) proposed a different scheme ·

$$2HNO_2 + SO_2 = H_2SNO_5 + NO.$$
$$H_2SNO_5 = H_2SO_4 + NO$$
$$2NO + H_2O + O = 2HNO_2$$

The concentration of sulphuric acid.—The chamber acid (65–70 per cent. H_2SO_4) may be used directly in the manufacture of superphosphate. Unless all the chamber acid is passed through the Glover tower, the remainder may be concentrated to 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 impurities. Stronger acid, 93–95 per cent. H_2SO_4, called " rectified oil of vitriol," or R.O.V., is made by concentration of B O.V. This was formerly carried out by heating in glass or platinum retorts, but is now effected in special concentration apparatus, *e g.* 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 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 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 furnace passes (Fig. 258). 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. In America, hot gases from a burning spray of petroleum are bubbled through the acid.

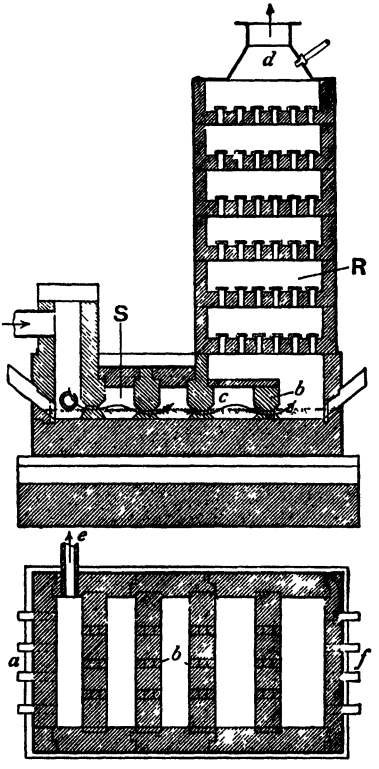


FIG 258 —Kessler apparatus for concentrating sulphuric acid

The **Gaillard tower** 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 furnace, which enters the tower at the side near the bottom. The acid is concentrated and runs out from a lead tray in which the tower stands, to a cooler

The acid fumes from concentrators may be condensed by means of electrostatic precipitation. 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 to be returned to the concentrators

Still more concentrated acid, containing 97–98 per cent. of H_2SO_4, is produced by heating 93–95 per cent. acid in pans by direct fire. The strongest acid does not attack cast iron, whilst 93–95 per cent acid dissolves it The acid is therefore run in a thin 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 free SO_3)

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 with hydrogen sulphide 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, a little paraffin added to the liquid floats to the surface and carries the precipitate with it. Acid made from sulphur ("brimstone acid") is preferred for the preparation of foods and for lead accumulators (in which acid free from iron salts is essential), although purified acid from pyrites is also used.

Oxides of nitrogen may be removed by strongly heating with a small quantity of ammonium sulphate

$$N_2O_3 + (NH_4)_2SO_4 = 2N_2 + H_2SO_4 + 3H_2O$$

The commercial acid usually contains lead sulphate, most of which is deposited on dilution with water.

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, from free sulphur trioxide formed by dissociation in the liquid ·

$$H_2SO_4 \rightleftharpoons SO_3 + H_2O.$$

This dissociation increases on heating and the vapour is richer in SO_3 than the residual liquid. It is therefore impossible to obtain the pure acid by the ordinary concentration process. The monohydrate freezes in ice and salt, and the crystals then melt at 10·49°. On boiling, an acid of constant composition, 98·3 per cent. H_2SO_4, comes over at a temperature of 338°, which is usually given as the boiling point of sulphuric acid. The 95 per cent. acid boils at 295°. The ordinary acid (98 per cent. H_2SO_4) is a colourless oily liquid, sp. gr. 1·84, which does not fume.

Concentrated sulphuric acid is very corrosive, and has a strong affinity for water: when mixed with water a considerable amount of heat is given out, and the liquid may boil. In practice, the acid

should always be added to the water in a thin stream, with stirring, never the water to the acid. The diluted acid occupies a smaller volume than its constituents, and the contraction is a maximum for $H_2SO_4 + 2H_2O$.

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 hydrates, H_2SO_4,H_2O, $H_2SO_4,2H_2O$, and $H_2SO_4,4H_2O$ may exist in a partly 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 at 15° are given in the table below: 97·7 per cent acid has a maximum density of 1 8415

TABLE OF DENSITIES OF SULPHURIC ACID.

Per cent H_2SO_4	Density	Per cent H_2SO_4	Density.
1·0	1 0161	60	1 5024
5	1·0332	65	1 5578
10	1·0681	70	1 6151
15	1 1045	75	1 6740
20	1·1412	80	1·7324
25	1·1816	85	1·7841
30	1·2220	90	1 8198
35	1 2636	95	1 8388
40	1 3065	97	1 8415
45	1 3514	98	1·8411
50	1·3990	99	1 8393
55	1·4494	100	1·8384

TABLE OF DENSITIES OF OLEUM AT 15°.

Per cent free SO_3	Density	Per cent free SO_3	Density.
10	1·888	60	2·020
20	1 920	70	2·018
30	1 957	80	2 008
40	1·979	90	1·990
50	2·009	100	1·984

These tables show that, at higher strengths, the density does not enable one to find the concentration of the acid. The density of oleum is a maximum for 60 per cent free SO_3.

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 conveniently used by boiling pieces of pumice with the acid; the lumps of impregnated pumice are placed in a glass tower.

The affinity of the acid for water is also shown by the charring of organic matter containing carbon, hydrogen, and oxygen. The elements of water are removed and black carbon is left.

EXPT 9.—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

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 platinum or quartz tube, the sulphur trioxide is decomposed into oxygen and sulphur dioxide, which do not recombine on cooling . $2H_2SO_4 = 2SO_2 + O_2 + 2H_2O$.

In aqueous solution sulphuric acid is 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, the acid and normal, are known, corresponding with the formulae $RHSO_4$ and R_2SO_4. Many of the normal 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 those of lead, calcium, and strontium are sparingly soluble ; barium sulphate is practically insoluble in water and dilute acids, and its formation is used as a test for sulphuric acid or sulphates. A solution of barium chloride is added to the liquid to be tested, together with 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 solubility product action of the chloride ion, but readily dissolves in water. In the estimation of sulphuric acid or sulphates, the boiling solution is mixed with a boiling solution of barium chloride. The precipitated $BaSO_4$ is then readily filtered.

Concentrated sulphuric acid is reduced to sulphur dioxide by hydrogen, especially when heated, and by heated carbon and sulphur. Phosphorus decomposes the heated acid, with formation of sulphur dioxide and sulphur : the phosphorus is oxidised to phosphorous and phosphoric acids.

Many metals (Mg, Zn, Fe, etc.) dissolve in the *dilute* acid with liberation of hydrogen Sodium, potassium and magnesium liberate hydrogen from the cold concentrated acid Most metals dissolve in the hot concentrated acid with evolution of sulphur dioxide; iron liberates hydrogen and sulphur dioxide on heating, but the action soon ceases With the hot concentrated acid, zinc gives sulphur dioxide, with somewhat diluted acid, hydrogen sulphide. Lead is attacked by the hot very concentrated acid (the perfectly pure metal is more resistant) tin and antimony are dissolved.

The reduction to sulphur dioxide by metals has been represented by two sets of equations, in which M is a bivalent metal:

$$(1)\quad H_2SO_4 + M = MSO_4 + H_2;$$
$$H_2SO_4 + H_2 = 2H_2O + SO_2.$$
$$(2)\quad H_2SO_4 + M = MO + SO_2 + H_2O;$$
$$H_2SO_4 + MO = MSO_4 + H_2O.$$

Alkali metal (except ammonium) sulphates and those of lead and magnesium are stable on heating, except at very high temperatures; those of zinc, copper and iron at high temperatures evolve SO_3, SO_2 and oxygen; calcium sulphate is decomposed at a high temperature, whilst strontium and barium sulphates are stable Most sulphates are reduced to sulphides by heating in a current of hydrogen, or with carbon·

$$K_2SO_4 + 4H_2 = K_2S + 4H_2O;$$
$$Na_2SO_4 + 2C = Na_2S + 2CO_2;$$
$$BaSO_4 + 4C = BaS + 4CO.$$

Silver sulphate is reduced to the metal:

$$Ag_2SO_4 + 2H_2 = 2Ag + SO_2 + 2H_2O;$$

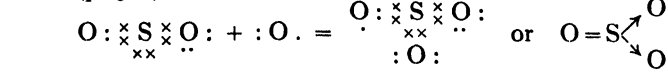
aluminium and chromium sulphates form the oxides:

$$Al_2(SO_4)_3 + 3H_2 = Al_2O_3 + 3SO_2 + 3H_2O.$$

Many sulphates are decomposed when heated in a current of hydrogen chloride·

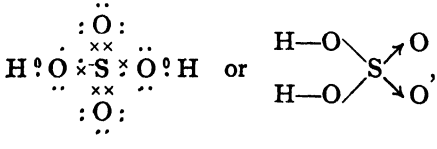
$$2CuSO_4 + 4HCl = 2CuCl_2 + 2SO_2 + 2H_2O + O_2.$$

The electronic formula of sulphur trioxide may be written by adding an atom of oxygen to the lone pair of electrons on the sulphur in the dioxide (p. 506):



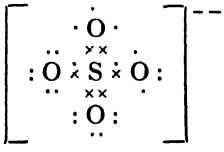
or

Sulphuric acid and the sulphate ion are represented as:



or

and



The chlorides of sulphuric acid.—When sulphuric acid is mixed with phosphorus pentachloride, hydrogen chloride is evolved and two compounds are formed which have the formulae SO_3HCl and SO_2Cl_2:

$$SO_2(OH)_2 + PCl_5 = SO_2(OH)Cl + POCl_3 + HCl,$$
$$SO_2(OH)Cl + PCl_5 = SO_2Cl_2 + POCl_3 + HCl.$$

The three substances may be separated by fractional distillation, since their boiling points are quite different; $POCl_3$, 107·2°; $SO_2(OH)Cl$, 151°–152°; SO_2Cl_2, 69·1°

The compound $SO_2(OH)Cl$ is known as **chlorosulphonic acid**; and SO_2Cl_2 as **sulphuryl chloride.** They belong to the general class of acid chlorides, formed by exchange of hydroxyl groups in oxy-acids for chlorine, and with water are reconverted into the original acids:

$$SO_2(OH)Cl + H_2O = SO_2(OH)_2 + HCl,$$
$$SO_2Cl_2 + 2H_2O = SO_2(OH)_2 + 2HCl.$$

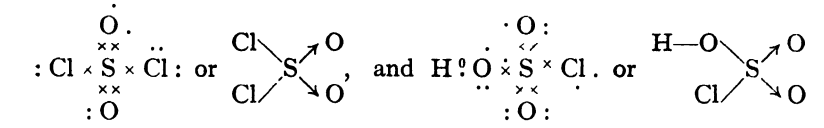
Chlorosulphonic acid may be obtained by the direct combination of sulphur trioxide and hydrogen chloride: $SO_3 + HCl = SO_3HCl$, or by the action of phosphorus pentachloride on sulphuric acid, as explained above. Since an excess of phosphorus pentachloride produces sulphuryl chloride, phosphorus oxychloride, $POCl_3$, may be used, as this does not interact further with chlorosulphonic acid: $2SO_2(OH)_2 + POCl_3 = 2SO_2(OH)Cl + HPO_3 + HCl$. Chlorosulphonic acid is obtained on the large scale by passing dry hydrogen chloride through fuming sulphuric acid (containing SO_3), and distilling. It is a colourless fuming liquid, sp. gr. 1·753/20°, violently decomposed by water, producing sulphuric and hydrochloric acids. At 170°–190° it decomposes into SO_2Cl_2 and H_2SO_4, at higher temperatures into Cl_2, SO_2, and H_2O. It reacts violently with silver nitrate, forming nitrososulphuric acid:

$$2SO_2(OH)Cl + 2AgNO_3 = 2AgCl + 2SO_2(OH)O{\cdot}NO + O_2$$

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, acetic anhydride, or animal charcoal: $SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$; also by the prolonged action of phosphorus pentachloride on sulphuric acid, or by heating chlorosulphonic acid in a sealed tube at 180°: $2HClSO_3 = SO_2Cl_2 + H_2SO_4$ It may be produced by a modification of the last reaction, by heating in a flask under a reflux condenser heated to 70°, a mixture of chlorosulphonic acid with 1 per cent. of mercuric sulphate which acts as a catalyst, and condensing the vapour

Sulphuryl chloride is a colourless fuming liquid, sp. gr. 1·667 at 20°, which boils at 69° without decomposition. It is rather slowly 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, $SO_2Cl_2,5H_2O$. The electronic formulae of sulphuryl chloride and chlorosulphonic acid follow from that of sulphuric acid (p 519):



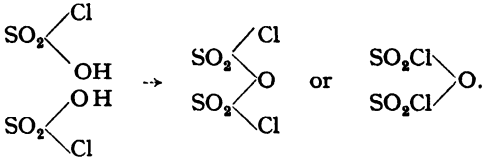
The chloride of pyrosulphuric acid, **pyrosulphuryl chloride**, $S_2O_5Cl_2$, is obtained by the action of sulphur trioxide on thionyl chloride or on sulphur chloride

$$SOCl_2 + 2SO_3 = S_2O_5Cl_2 + SO_2,$$
$$5SO_3 + S_2Cl_2 = 5SO_2 + S_2O_5Cl_2,$$

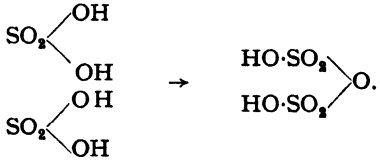
or by the action of sulphur trioxide or chlorosulphonic acid on phosphorus pentachloride

$$2SO_3 + PCl_5 = POCl_3 + S_2O_5Cl_2,$$
$$2SO_2(OH)Cl + PCl_5 = POCl_3 + 2HCl + S_2O_5Cl_2$$

It is a heavy mobile liquid, sp gr 1·844/18°, boiling at 57° at 30 mm, or 150·7° under 730 mm pressure, giving a nearly normal vapour density, although some decomposition into sulphur dioxide, sulphur trioxide and chlorine occurs. 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 $S_2O_5(OH)_2$, 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**.

Fluosulphonic acid, $SO_2(OH)F$, b. pt. 162·6°, is obtained by heating fluorspar with fuming sulphuric acid in an iron retort. **Sulphuryl**

fluoride, SO_2F_2, b. pt. $-52°$, is obtained as a very stable and inert gas by heating barium fluosulphonate

$$Ba(SO_3F)_2 = BaSO_4 + SO_2F_2$$

Negative groups.—Although all acids contain hydrogen, 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, *e.g.*, sodamide, $NaNH_2$. Hydrogen atoms in hydrocarbons may also, by indirect means, be replaced by metals, forming **organo-metallic compounds**; 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 ionisable in solution and is neutralised by hydroxides, and this is equivalent to saying that acidic hydrogen is that which can form hydrogen ions, the latter uniting with hydroxyl to form water: $H + OH' \rightleftharpoons H_2O$, or with other bases to form stable complexes, *e.g.*, $NH_4^{\cdot}$ with NH_3

The acidic character of certain hydrogen compounds is determined by the character of the rest of the molecule. In the halogen hydracids, for example, hydrogen is united with a *strongly electronegative atom* of halogen, and strong acids result. In H_2S, hydrogen is united with the weakly electronegative atom of sulphur, to form a very weak acid. The case of water, H_2O, is exceptional, since it combines both acid and basic functions, ionising into H 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 The molecule $SO_2(OH)_2$ may be regarded as formed by the replacement of 2 atoms of hydrogen from 2 molecules of water by the bivalent negative sulphuryl radical $=SO_2$ 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 due to the presence of a **negative group**, *e.g.*, $=SO_2$, in the molecule Such a group tends to attract an electron from a hydrogen atom in the molecule, and the hydrogen nucleus or proton is then capable of leaving the molecule as a hydrogen ion. In organic acids the negative group is uniformly the **carbonyl group**, —CO— : acetic acid is $CH_3{\cdot}CO{\cdot}OH$ and oxalic acid is $(CO{\cdot}OH)_2$.

Hantzsch (1917) found that the absorption spectra of esters of nitric acid, such as $C_2H_5NO_3$, are all alike, as are those of metal salts such as KNO_3 in solution, but the two sets of spectra are different. The spectrum of the concentrated acid resembles that of the esters, but when the acid is diluted the spectrum gradually changes to that of the

salt. He considers that nitric acid and other oxy-acids exist in two tautomeric forms in equilibrium

I. *Pseudo-form* :	II *Normal form* ·
Concentrated acid and esters.	Dilute acid and metal salts
Non-ionisable	Hydrogen is ionisable (in the " outer sphere ").
Weaker absorption.	Stronger absorption

The " loosely held " hydrogen in the normal form is supposed to be capable of exhibiting acidic properties even though it is not actually ionised, *e g* , it can act as a catalyst

The " hydrogen ion " formed in aqueous solutions of acids is really H_3O , formed by the association of a proton, produced from the acid by ionisation, with a molecule of water, the proton attaching itself to the lone pair of electrons on the oxygen

$$H^+ + H \times O \times H = H \times O \times H$$
$$\qquad\qquad\qquad\qquad\qquad\quad H^+$$

In solvents not containing suitable receptor atoms, acids do not ionise

Hydroxyl combined with a **positive group,** such as an atom of metal or a radical such as ammonium, NH_4, ionises as such and the compound shows basic properties. The more strongly electropositive is the metal or radical, the stronger is the base · KOH is a strong base, $Al(OH)_3$ is a weak base.

If the electropositive group is only weak, the compound may also show weakly acidic properties $Al(OH)_3$ behaves either as a weak base or as a weak acid, according as it is treated with a strong acid or a strong base · $Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$; $Al(OH)_3 + KOH = KAlO_2 + 2H_2O$ Such a substance is called an **amphoteric electrolyte,** or an **ampholyte** ; the acidic and basic properties are very weak and practically evenly balanced.

Persulphuric Acids.

Persulphuric acids.—Faraday (1834) when electrolysing a concentrated aqueous solution of sulphuric acid, observed that " a remarkable disappearance of oxygen took place," but thought this was due to the formation of hydrogen peroxide 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 supposed by Berthelot to be **persulphuric anhydride,** S_2O_7, but according to Meyer, Bailleul and Henkel (1922) they consist of a mixture of SO_3 and SO_4. Marshall (1890) found that on electrolysis of a concentrated solution of potassium hydrogen sulphate, $KHSO_4$, crystals of the composition KSO_4 separate at the anode.

In Faraday's experiment persulphuric acid is formed from the HSO_4' ions discharged at the anode $H_2SO_4 \rightleftharpoons H + HSO_4'$, $2HSO_4 = H_2S_2O_8$, although the anodic reaction is now considered to be: $2HSO_4' + H_2O + O = H_2S_2O_8 + 2OH'$. The doubled formula of the potassium salt is found by the freezing-point and conductivity methods.

EXPT 10.—Persulphuric acid is formed by the electrolysis of 50 per cent sulphuric acid with an anode formed of a platinum wire, surrounded by a glass tube to serve as a diaphragm. The cathode consists of a spiral of copper wire outside the diaphragm (Fig. 259). The apparatus is immersed in ice. The addition of a little hydrochloric acid promotes the reaction. If a saturated potassium hydrogen sulphate solution is used crystals of the persulphate separate out. The solution in each experiment gives a brown colour with potassium iodide:

$$H_2S_2O_8 + 2KI = 2KHSO_4 + I_2$$

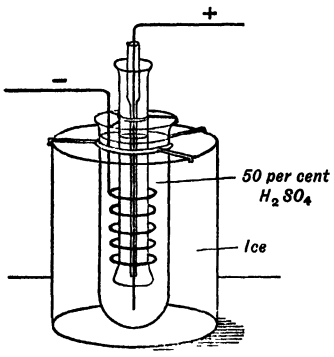


FIG. 259.—Preparation of persulphuric acid

In the preparation of potassium persulphate, the ions HSO_4' are discharged, and persulphuric acid is formed. This reacts with the potassium hydrogen sulphate, and the sparingly soluble persulphate crystallises out

$$H_2S_2O_8 + 2KHSO_4 \rightleftharpoons K_2S_2O_8 + 2H_2SO_4.$$

Persulphates are powerful oxidising agents. Besides slowly liberating iodine from iodides, they oxidise ferrous salts to ferric salts. $2FeSO_4 + K_2S_2O_8 = Fe_2(SO_4)_3 + K_2SO_4$. The ammonium salt, $(NH_4)_2S_2O_8$, prepared in a similar way to 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, BaS_2O_8, is very soluble in water and serves to separate persulphuric acid from sulphuric acid. On boiling, the solution deposits barium sulphate.

Potassium persulphate is decomposed by heat: $2K_2S_2O_8 = 2K_2SO_4 + 2SO_3 + O_2$, the solution decomposes slowly in the cold, but rapidly on warming, with evolution of ozonised oxygen. $2K_2S_2O_8 + 2H_2O = 4KHSO_4 + O_2$. Chromic salts in alkaline solution are oxidised to chromates. Manganese, cobalt, nickel and lead salts in presence of alkali are oxidised to peroxides. $Mn(OH)_2 + K_2S_2O_8 + H_2O = 2KHSO_4 + MnO_2 + H_2O$. Silver nitrate gives with potassium (*not* ammonium) persulphate a black precipitate of silver peroxide.

$$2AgNO_3 + K_2S_2O_8 + 2H_2O = 2KHSO_4 + 2HNO_3 + Ag_2O_2 \text{ (Marshall).}$$

Caro in 1898, by dissolving potassium persulphate in concentrated sulphuric acid, obtained a solution of a persulphuric acid which is a powerful oxidising agent, converting aniline into nitrosobenzene, whilst Marshall's acid gives aniline black. Baeyer and Villiger, in 1901, prepared **Caro's acid** 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. Marshall's acid, Caro's acid, and hydrogen peroxide are distinguished by the following reactions :

1. Caro's acid instantly liberates iodine from iodides
2. Marshall's acid only slowly liberates iodine from iodides.
3. Hydrogen peroxide at once reduces potassium permanganate, which is not changed by persulphuric acids.

In the solution they determined the ratio SO_3 . peroxide O, which was found to be 1 1 , hence the formula of Caro's acid is $SO_3 + O + H_2O$, or H_2SO_5 Free **permonosulphuric acid** was prepared in a nearly pure state by Ahrle (1909) by the action of sulphur trioxide on very concentrated hydrogen peroxide $SO_3 + H_2O_2 = H_2SO_5$ The reaction with concentrated sulphuric acid is reversible $H_2SO_4 + H_2O_2 \rightleftharpoons H_2SO_5 + H_2O$ Hydrogen peroxide is manufactured by distilling persulphuric acid solution obtained by the electrolytic oxidation of sulphuric acid, under reduced pressure. D'Ans and Friedrich (1910) prepared both Caro's and Marshall's acids in the pure state by the action of hydrogen peroxide on chlorosulphonic acid :

$$HO{\cdot}SO_2{\cdot}Cl + HO{\cdot}OH = HO{\cdot}SO_2{\cdot}O{\cdot}OH + HCl;$$
$$HO{\cdot}SO_2{\cdot}Cl + HO{\cdot}O\,SO_2{\cdot}OH = HO\,SO_2{\cdot}O\,O{\cdot}SO_2\,OH + HCl.$$

Caro's acid is crystalline, melts at 45°, and is stable for some days $H_2S_2O_8$ 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 permonosulphuric acid is seen by the above reactions to be $HO\,O{\cdot}SO_2{\cdot}OH$, that of **perdisulphuric acid**, or the ordinary acid, is $HO{\cdot}SO_2\,O{\cdot}O{\cdot}SO_2\,OH$. These formulae agree with the constitution adopted for hydrogen peroxide.

Thiosulphuric and Thionic Acids.

Thiosulphuric acid.—When a solution of sodium sulphite is boiled with flowers of sulphur in absence of air, a salt separates on evaporation and cooling in large monoclinic crystals, which have the formula $Na_2S_2O_3{,}5H_2O$: $Na_2SO_3 + S = Na_2S_2O_3$. The compound $Na_2S_2O_3$ may be regarded as sodium sulphate in which an oxygen atom is replaced by one of sulphur, and hence it is known as **sodium thiosulphate.** The crystalline salt, used in photography, is commonly called sodium "hyposulphite" (or "hypo"), but this name belongs chemically to the compound $Na_2S_2O_4$. Pure sodium thiosulphate and especially potassium thiosulphate ($3K_2S_2O_3{,}5H_2O$) are best prepared by the

interaction of alkali hydrogen sulphides and hydrogen sulphites in solution, and crystallising :

$$2KHS + 4KHSO_3 = 3K_2S_2O_3 + 3H_2O.$$

The formula of sodium sulphite may be either symmetrical or unsymmetrical, NaO·SO ONa or $Na{\cdot}SO_2{\cdot}ONa$. The second is considered more probable, hence the formula of the thiosulphate is $NaS{\cdot}SO_2{\cdot}ONa$, analogous to that of the sulphate, $NaO{\cdot}SO_2{\cdot}ONa$.

Spring showed that if the thiosulphate is treated with sodium amalgam and water, sodium sulphite and sodium sulphide are produced : $NaO\ SO_2\ SNa + 2Na = NaO{\cdot}SO, Na + Na_2S$. If silver thiosulphate is boiled with water a black precipitate of silver sulphide is produced .

$$SO_2(OAg)(SAg) + H_2O = SO_2(OH)_2 + Ag_2S.$$

By the action of ethyl bromide on a concentrated solution of sodium thiosulphate, sodium ethyl thiosulphate is formed

$$C_2H_5Br + Na_2S_2O_3 = C_2H_5NaS_2O_3 + NaBr$$

When warmed with hydrochloric acid this is hydrolysed to ethyl hydrogen sulphide or mercaptan, C_2H_5SH, in which the ethyl group is directly attached to sulphur (Bunte, 1874)

$$NaO\ SO_2\ SC_2H_5 + HOH = NaO\ SO_2\ OH + HSC_2H_5.$$

Sodium thiosulphate was formerly made by oxidising alkali waste containing calcium sulphide, CaS, by exposure to air, and then precipitating the calcium thiosulphate solution formed with sodium carbonate.

When a solution of a sulphide is exposed to air, a complicated series of reactions occurs Polysulphides, free sulphur, thiosulphate and sulphate may all be formed, according to the conditions of the reaction, *e g* ,

$$12CaS + 9H_2O + 6O_2 = 9Ca(OH)_2 + CaS_2O_3 + 2CaS_5 ;$$
$$2CaS_5 + 3O_2 = 2CaS_2O_3 + 6S$$

Sodium thiosulphate is formed by the action of oxygen or sulphur dioxide on heated sulphides .

$$2NaHS + 2O_2 = Na_2S_2O_3 + H_2O ;$$
$$2Na_2S + 3SO_2 = 2Na_2S_2O_3 + S$$

If sulphur is boiled (or fused) with a caustic alkali, or milk of lime, a thiosulphate is produced as well as a sulphide or polysulphide :

$$6NaOH + 4S = Na_2S_2O_3 + 2Na_2S + 3H_2O.$$

Liver of sulphur (*hepar sulphuris*), a dark-brown mass formed by fusing potassium carbonate with sulphur, contains potassium sulphides and thiosulphate. 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. $Na_2SO_3 + S = Na_2S_2O_3$

Sodium thiosulphate crystals melt at 48°; on heating, the salt loses water at 215° and above 223° it decomposes.

$$4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5$$

At higher temperatures the Na_2S_5 loses sulphur.

If a solution of sodium thiosulphate is acidified, free **thiosulphuric acid,** $H_2S_2O_3$ (which is unknown in the pure state), is probably first formed but decomposes into sulphurous acid and free sulphur, which slowly deposits as a white turbidity · $H_2S_2O_3 = H_2SO_3 + S$. The reaction is really more complicated, and thionic acids are formed.

Sodium thiosulphate readily dissolves silver chloride bromide and iodide, forming a double salt which has a sweet taste, $Na_5[Ag_3(S_2O_3)_4] + 3H_2O$. 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 ")

Thiosulphates are readily oxidised by chlorine or bromine water · tetrathionate, sulphate, and some trithionate are formed, and sulphur is precipitated With a large excess of halogen, some sulphur is slowly oxidised to sulphuric acid Sodium thiosulphate is used as an *antichlor* to remove traces of chlorine from bleached fabrics. Potassium permanganate in *neutral* solution oxidises thiosulphate to sulphate: $2KMnO_4 + Na_2S_2O_3 = K_2SO_4 + Na_2SO_4 + Mn_2O_3$. In *acid* solution some dithionate is also formed.

Tetrathionic acid—On adding a solution of sodium thiosulphate to a solution of iodine, the colour of the latter is discharged. This reaction 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 salt of the formula $Na_2S_4O_6$, **sodium tetrathionate,** discovered by Fordos and Gélis in 1843. The reaction is quantitative: $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$, or $2S_2O_3'' + I_2 = S_4O_6'' + 2I'$. 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, with shaking after each addition, until only a pale yellow colour remains. The tetrathionate separates as crystals; it is washed with alcohol, dissolved in water, reprecipitated 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.

When 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 $2PbS_2O_3 + I_2 = PbI_2 + PbS_4O_6$, which on precipitation with dilute sulphuric acid gives a solution of free **tetrathionic acid**, $H_2S_4O_6$. The solution may be concentrated on a water-bath, and is fairly stable up to a certain point, with further concentration, 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 $Na_2S_4O_6 + 2Na = 2Na_2S_2O_3$ Tetrathionates give with sulphides a precipitate of sulphur $Na_2S_4O_6 + Na_2S = 2Na_2S_2O_3 + S$

On adding ferric chloride to a solution of sodium thiosulphate, a violet colour due to the complex anion $Fe(S_2O_3)_2'$ is first produced. This rapidly disappears and a colourless solution containing tetrathionate (together with some sulphate) is formed $Fe(S_2O_3)_2' + Fe = 2Fe^{\cdot} + S_4O_6''$, or in total $2Na_2S_2O_3 + 2FeCl_3 = 2NaCl + 2FeCl_2 + Na_2S_4O_6$.

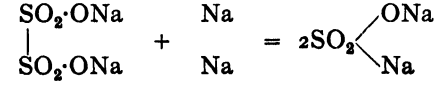
Dithionic acid.—If finely-ground *pyrolusite* (native crystalline manganese dioxide) is suspended in water and sulphur dioxide slowly passed in, the liquid being cooled in ice, the manganous salt of a new acid is formed (Gay-Lussac and Welter, 1819) When all the pyrolusite has reacted, baryta water is added until all the manganese is precipitated as hydroxide, and the sulphate also formed in the reaction is precipitated as barium sulphate. The excess of baryta is precipitated by a current of carbon dioxide, the liquid is filtered, and on evaporation colourless crystals of **barium dithionate**, $BaS_2O_6,2H_2O$, separate.

Manganic sulphite is first formed, and then decomposes as follows:

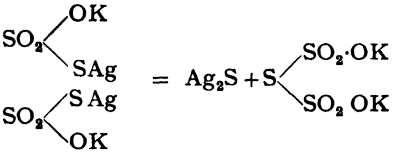
$$2MnO_2 + 3H_2SO_3 = Mn_2(SO_3)_3 + 3H_2O + O.$$
$$Mn_2(SO_3)_3 = MnS_2O_6 + MnSO_3.$$
$$MnSO_3 + O = MnSO_4.$$
$$MnS_2O_6 + Ba(OH)_2 = Mn(OH)_2 + BaS_2O_6$$
$$MnSO_4 + Ba(OH)_2 = Mn(OH)_2 + BaSO_4.$$

By decomposing the barium salt with the calculated amount of sodium carbonate, the sodium salt is obtained; from the barium salt and dilute 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 potassium salt of **trithionic acid,** $K_2S_3O_6$.



The same salt is formed by passing sulphur dioxide through a solution of potassium thiosulphate 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 on standing

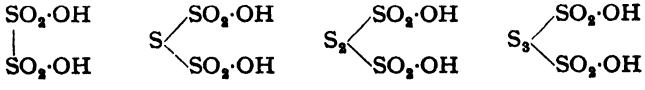
Pentathionic acid.—If hydrogen sulphide is slowly passed through a solution of sulphurous acid, colloidal sulphur is precipitated, and the milky liquid, known as **Wackenroder's solution** (1845), contains **pentathionic acid,** $H_2S_5O_6$ If it is treated with one-third of an equivalent of caustic potash, or with potassium acetate, 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, considered by Debus to be 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. Wackenroder's solution contains, in addition to these two thionic acids, sulphuric acid and a trace of trithionic acid.

Potassium hexathionate may be obtained (Weitz and Achterberg, 1928) by the addition of a solution of 1 mol of potassium nitrite and 3 mols of potassium thiosulphate to well cooled hydrochloric acid in a large flask, with vigorous shaking. The oxides of nitrogen are removed by a current of air and the solution cooled in a freezing mixture Potassium chloride separates and is removed. On concentrating the solution under reduced pressure, potassium hexathionate crystallises out

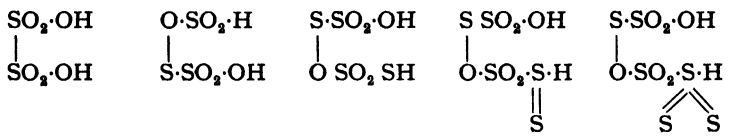
The reactions leading to formation of Wackenroder's solution have been represented as follows by Debus (1888):

$$H_2S + 2SO_2 = 3SO + H_2O\ ;$$
$$5SO + H_2O = H_2S_5O_6.$$

The formulae of the thionic acids proposed by Mendeléeff and Blomstrand (1870) are



The alternative formulae proposed by Debus are ·



Hertlein (1896) found that the polythionates of mercury and silver do not form complex compounds, and he considered that the metal is attached to oxygen as in Blomstrand and Mendeléeff's formulae, rather than to sulphur as in Debus's formulae, since these metals in combination with sulphur readily form complex compounds (p 859). Tetrathionic acid, $HO{\cdot}SO_2{\cdot}S{\cdot}S\ SO_2\ OH$, also corresponds with persulphuric acid, $HO\ SO_2{\cdot}O{\cdot}O{\cdot}SO_2{\cdot}OH$, and the tetrathionates form compounds with ammonia, etc., similar to those formed by persulphates, *e.g.*, $ZnS_4O_6{,}4NH_3$

Hyposulphurous acid.—By the action of zinc dust on 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 the zinc salt of hyposulphurous acid, $H_2S_2O_4$; the solution is a powerful bleaching and reducing agent. It bleaches indigo solution, reduces a solution of copper sulphate to a precipitate of cuprous hydride, Cu_2H_2, or copper, and precipitates mercury and silver from their salts. The moist compound rapidly absorbs oxygen from the air, forming a sulphite.

Sodium hyposulphite (formerly called hydrosulphite), $Na_2S_2O_4$, discovered by Schonbein in 1852 and by Schutzenberger in 1869, is prepared by treating a cooled concentrated solution of $NaHSO_3$ with zinc dust in a corked flask. Sulphur dioxide in the proportion shown below is passed in. Milk of lime is then added to precipitate the zinc sulphite also formed:

$$2NaHSO_3 + SO_2 + Zn = Na_2S_2O_4 + ZnSO_3 + H_2O\ ;$$
$$ZnSO_3 + Ca(OH)_2 = ZnO + CaSO_3 + H_2O.$$

The filtrate is warmed, saturated with sodium chloride, and allowed to cool, when thin vitreous prisms of $Na_2S_2O_4{,}2H_2O$ separate. These are washed with aqueous, then with anhydrous, acetone, and dried over concentrated sulphuric acid. 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, forming a sulphite.

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, explosion occurs.

The free acid is formed as a yellow solution by adding oxalic acid to a solution of the sodium salt. It rapidly decomposes, thiosulphuric acid being first formed and then decomposing into sulphurous acid and sulphur. In solution in absence of oxygen, especially on warming, the salts rapidly decompose.

$$2Na_2S_2O_4 = Na_2S_2O_3 + Na_2S_2O_5.$$

In presence of oxygen, the solutions are rapidly oxidised.

$$2Na_2S_2O_4 + O_2 = 2Na_2S_2O_5.$$

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-blue, $C_{16}H_{10}N_2O_2$, 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 Sodium hyposulphite is an important salt in colour chemistry.

Sulphoxylic acid, H_2SO_2, is known only in solution in the form of the zinc salt $2Zn + SO_2Cl_2 = ZnSO_2 + ZnCl_2$, and in an organic compound with formaldehyde $H{\cdot}COH,NaHSO_2,2H_2O$. Hyposulphurous acid may be regarded as the mixed anhydride of sulphurous and sulphoxylic acids:

$$H{\cdot}SO_2{\cdot}OH + HO{\cdot}SO{\cdot}H = H{\cdot}SO_2{\cdot}SO{\cdot}OH + H_2O.$$

Sulphur sesquioxide.—If flowers of sulphur are added to fused sulphur trioxide at 10°, blue drops are formed, which solidify to bluish-green crystalline crusts. This substance is **sulphur sesquioxide,** S_2O_3. It decomposes into sulphur and sulphur dioxide $2S_2O_3 = 3SO_2 + S$ (Vogel, 1812; Weber, 1875, I. Vogel and Partington, 1925) A blue liquid is produced by dissolving sulphur in fuming sulphuric acid (Bucholz, 1804). Water decomposes the sesquioxide with separation of sulphur and formation of sulphuric and thiosulphuric acids. The oxide does not give hyposulphurous acid, $H_2S_2O_4$, with water, as might be expected from its formula. The solution of the sesquioxide in fuming sulphuric acid is used in the manufacture of thiopyronin dyes.

CHAPTER XXVIII

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 (Latin *tellus*, the earth).

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; *zorgite* (Argentine), copper and lead selenides with as much as 31 per cent Se; 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 commercial sulphuric acid In making salt-cake with this acid, the selenium passes over into the hydrochloric acid, from which the element deposits in the first receivers in the form of a red powder. To prepare selenium from the deposit, 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 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 electrolytic copper refining, which may contain as much as 96 per cent. of the element together with tellurium, although 1 to 18 per cent Se and 0·25 to 2·5 per cent. Te are the usual proportions. Selenium is used in making red glass, red enamels and glazes.

Forms of Selenium.—Various modifications of selenium are known: according to Saunders (1900) these fall into three main groups:—

1. **Amorphous selenium.** 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*) *Red amorphous selenium*, a dark 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. Amorphous selenium dissolves slightly in carbon disulphide

2. **Monoclinic 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. 489).

3. **Metallic selenium** is formed when any other variety is heated at 200°–220° for some time. It is a silvery-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) but is soluble in chloroform

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°C.	-	-	774	815	900–1800
Δ(H = 1)	-	-	101·2	95 4	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 resistance is recovered after a short time. This effect, which is utilised in the selenium cell 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. A form A, obtained on heating vitreous Se at 170°, consisting of round granular crystals, is an insulator. Form B, produced when A is heated for some time at 200°, forms longer crystals and is a conductor, the conductivity increasing greatly on exposure to light, probably by liberation of electrons in the mass (inner photoelectric effect)

Hydrogen selenide.—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 normal density of the gas is 3·6696, and it leaves its own volume of hydrogen when decomposed by heated tin; hence the formula is H_2Se It liquefies at $-41·7°$, 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 **monochloride**, 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 pale-yellow solid by treating selenium with excess of 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 yellow vapour is dissociated: $2SeCl_4 \rightleftharpoons Se_2 + 4Cl_2$ (Evans and Ramsay), or $2SeCl_4 \rightleftharpoons Se_2Cl_2 + 3Cl_2$ (Chabrié). 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**, $SeOCl_2$, b. pt. 177·2°, is formed. Se_2Br_2 and $SeBr_4$ are known, but no iodides.

Oxide and oxy-acids of selenium.—Selenium burns in oxygen with a blue flame, producing a crystalline dioxide, SeO_2. A trace of hydrogen selenide is produced during the combustion of selenium in moist air; it possesses a strong odour of rotten horseradish. A similar smell is emitted when selenium is heated on charcoal before the blowpipe.

If the dioxide is dissolved in water, or selenium boiled with nitric acid, colourless very soluble prismatic crystals of **selenious acid**, H_2SeO_3, separate on evaporation. It is dibasic, forming acid and normal salts, *e.g.*, $KHSeO_3$ and K_2SeO_3. Superacid salts are also formed: $KHSeO_3,H_2SeO_3$ It is readily reduced (*e.g.*, by organic matter in dust) with deposition of red selenium. Potassium permanganate oxidises selenious to selenic acid.

Selenium trioxide, SeO_3, is unknown, 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: $Ag_2SeO_3 + H_2O + Br_2 = 2AgBr + H_2SeO_4$; by oxidising selenium dioxide with chloric acid, 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, when it decomposes on further heating. If this

liquid is placed over sulphuric acid in a vacuum 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 selenium with nitre (Mitscherlich, 1827), and the sodium salt by heating selenium and sodium peroxide.

Heated selenic acid dissolves copper and gold, and is partly reduced to selenious acid. The dilute acid dissolves zinc, iron, etc , liberating hydrogen and forming selenates Barium selenate is sparingly soluble in water and acids, and occludes salts more readily than barium sulphate.

Selenic acid is not very easily reduced by sulphur dioxide or by hydrogen sulphide, but it is decomposed with formation of selenious acid by boiling with dilute hydrochloric acid. $H_2SeO_4 + 2HCl = H_2SeO_3 + Cl_2 + H_2O$ The solution then deposits selenium when treated with sulphur dioxide.

Selenium dissolves in fused sulphur trioxide, or oleum, the *green* compound $SSeO_3$ (**selenosulphur trioxide**) being formed (Sulphur gives *blue* S_2O_3, tellurium *bright red* $STeO_3$)

Selenium dissolves in potassium sulphite solution, giving a solution of the **selenosulphate**, K_2SSeO_3, which forms colourless crystals

Tellurium.—Tellurium occurs in small quantities in the free state, and was called by the early mineralogists *aurum paradoxum* or *metallum problematicum*, on account of its lustre. Muller von Reichenstein (1782) sent a small specimen of it to Bergman, who concluded that it was a peculiar metal similar to antimony 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 intermediate in its properties between the metals and non-metals.

Tellurium occurs only in relatively small quantities; native tellurium is found in Central Europe, America, and Bolivia, and with selenium in Japanese sulphur, but it 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.

Tellurium is usually extracted from the residues from bismuth ores. They are dissolved in hydrochloric acid, and sodium sulphite 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 6·31. 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 452·5°, and boils at 1390°; 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, and 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, *e.g.*, the basic nitrate, $2TeO_2,HNO_3$.

Hydrogen telluride.—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 at $-20°$ with a tellurium cathode, and at once drying and liquefying the gas, b. pt $-1·8°$, m. pt. $-57°$ 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, tellurium is deposited

Tellurium when fused with potassium cyanide does not form any compound analogous to KCNS or KCNSe, but only K_2Te.

Halogen compounds of tellurium.—With excess of chlorine the *stable* white crystalline **tetrachloride**, $TeCl_4$ (m. pt. 214°, b pt 414°) 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 from the elements in iron-grey crystals, also by the reaction $H_2TeO_3 + 4HI = TeI_4 + 3H_2O$. Gaseous TeF_6, and solid $TeBr_4$, are known.

Telluric acid.—**Tellurium trioxide**, TeO_3, obtained by heating telluric acid, H_2TeO_4, 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 hydrochloric acids, adding chloric acid in small portions, evaporating in a vacuum, precipitating 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 exists in several modifications. $Te(OH)_6$ exists in two crystalline forms; below 10° the solution deposits $H_2TeO_4,6H_2O$. It is difficultly soluble in cold water, but readily dissolves in hot water. It is a very weak acid. The methyl ester, $Te(OCH_3)_6$, and Ag_6TeO_6, are also known. When heated to 140°, H_6TeO_6 forms **allotelluric acid**, which is a fairly strong acid.

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*, $K_2TeO_4,TeO_3,4H_2O$; $K_2TeO_4,3TeO_3,4H_2O$) are known. Tellurates are reduced to tellurites on boiling with hydrochloric acid: $K_2TeO_4 + 2HCl = K_2TeO_3 + H_2O + Cl_2$, and are reduced by sulphur dioxide to tellurium (cf selenates). Barium tellurate, $BaTeO_4,3H_2O$, is fairly soluble in water.

If the red compound $STeO_3$ (p 535) is heated *in vacuo* to 230°, SO_2 is evolved and a 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 (1889) attempted to separate this, and found that the atomic weight was considerably higher when tellurium was merely fused in an indifferent gas than when it was distilled in hydrogen.

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. 260) 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 = 127·6 was obtained, which is higher than the atomic weight of iodine, I = 126·92. Flint (1909) claimed to have succeeded in separating fractions from tellurium by method (5), but this was not substantiated by Harcourt and Baker. Honigschmid (1933) found Te = 127·59 The isotopes of tellurium are 122, 123, 124, 126, 127 (?), 128 and 130. Iodine is a simple element and has only one kind of atom.

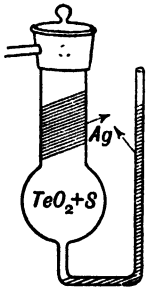


FIG 260.—Atomic weight of tellurium

Tellurium from Joachimsthal pitch-blende contains a trace of radium-F, or **polonium**, at. wt. 210 (Chap. XXV), precipitated from solution by bismuth.

CHAPTER XXIX

NITROGEN AND ITS COMPOUNDS WITH HYDROGEN

Nitrogen.—Scheele (1772) proved that air is a mixture of two gases, *fire air*, which supports combustion and respiration, and *foul air*, which does not Lavoisier (1775–6) furnished a decisive proof of this, and gave to Scheele's foul air the name azote (Greek *a*, no, *zoe*, life), still used in France; the name nitrogen (Greek *nitron*, nitre) was suggested by Chaptal in 1790.

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 considered that the gas was common air saturated with 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 inert gas, the existence of which had been suspected by Cavendish in 1785, was called **argon** (Greek *argon*, sluggish); later experiments showed that it contained 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 in 1783 found that the composition of pure dry air is sensibly constant: 20·833 vols. of oxygen and 79·167 vols. of nitrogen (including argon). The composition appears to be *slightly* variable: the percentage of oxygen varies according to the locality, etc., and at different times at the same place.

Traces of free nitrogen are found in volcanic gases and in the gases evolved from coal; the gases evolved from springs may contain over 95 per cent. by volume of nitrogen.

Nitrogen is a constituent of some important compounds. In combination with hydrogen it forms the base **ammonia**, NH_3, occurring in the free state and as salts in air, water, and volcanic products. In combination with oxygen, nitrogen forms **nitrous acid**, HNO_2, and **nitric acid**, HNO_3. 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.

Preparation of nitrogen from air.—Nitrogen may be prepared: (*a*) from atmospheric air by removal of oxygen, (*b*) from nitrogen compounds 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 nitrogen.

Oxygen is removed from air (previously freed from carbon dioxide) by the action of phosphorus, moist iron filings, liver of sulphur, etc., at the ordinary temperature. Phosphorus, an alkaline solution of pyrogallol, an acid solution of chromous chloride, or a solution of cuprous chloride in hydrochloric acid or ammonia: $4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O$, remove atmospheric oxygen completely Metallic copper in contact with hydrochloric acid or ammonia also removes the oxygen.

EXPT. 1.—Pack a drying tower 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)

EXPT. 2.—A long glass tube, sealed at one end and fitted with a rubber stopper, is divided into six equal volumes by labels A solution of pyrogallol is poured in so as to occupy one division. A *small* piece of solid caustic soda is slid into the upper part by means of crucible tongs, taking care that it does not fall into the liquid. The stopper is inserted

and the tube shaken. The liquid becomes black owing to absorption of oxygen. The tube is opened under water: one of the remaining five divisions fills with water, and four-fifths of the original volume of air remain as nitrogen.

Oxygen is also removed from air by burning phosphorus, but not quite completely.

EXPT. 3.—Float a porcelain capsule containing a piece of phosphorus on water, cover with a bell-jar divided from the water-level into five equal volumes by strips of waxed paper (Fig. 261), kindle the phosphorus with a hot wire, and 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.

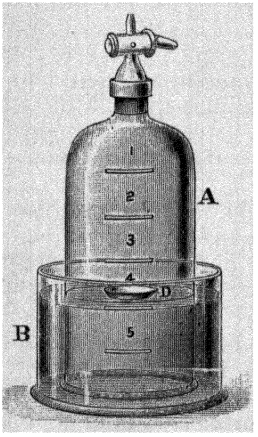


FIG. 261.—Burning phosphorus in air.

Oxygen is removed by passing air, dried and freed from carbon dioxide by solid caustic potash, over a long length of copper turnings heated to bright redness in a hard glass tube.

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 (Vernon Harcourt): $4NH_3 + 3O_2 = 2N_2 + 6H_2O$. The gas so prepared is a mixture of atmospheric and pure nitrogen: its density is intermediate between the densities of these two gases.

Nitrogen is made on the large scale either by passing air over red-hot copper, or mostly by the fractionation of liquid air (p. 143).

The volumetric composition of air.—The most *accurate method* of finding the percentage by volume of oxygen in air is to explode a measured volume of air with excess of hydrogen in a eudiometer over mercury. The hydrogen unites with the oxygen to form water, which condenses to a liquid of negligible volume, hence the volume of oxygen is found by taking *one third* of the measured contraction.

Since the residual gas is measured moist, the initial mixture of hydrogen and air should also be saturated with water vapour by passing a few drops of water into the eudiometer before measuring the gases.

The following results were found in an experiment by Bunsen :

Vol. of air	(at S.T.P.)	428·9 mm.
Vol. of air + H_2	,,	749·8 mm.
Vol. after explosion	,,	480·1 mm.

$\therefore$ vol. of oxygen $= (749{\cdot}8 - 480{\cdot}1)/3 = 89{\cdot}9$ mm. ;

$\therefore$ vol. of nitrogen $= 428{\cdot}9 - 89{\cdot}9 = 339{\cdot}0$ mm.

$$\therefore \text{ vol. of oxygen in 100 vols. air} = \frac{100}{428{\cdot}9} \times 89{\cdot}9 = 20{\cdot}9 ;$$

$\therefore$ vol. of nitrogen in 100 vols. air $= 100 - 20{\cdot}9 = 79{\cdot}1$;

$\therefore$ air contains 20·9 per cent. of oxygen and 79·1 per cent. of nitrogen (and argon) by volume.

The gravimetric composition of air.—The determination of the composition of air *by weight* is carried out by the method of Dumas

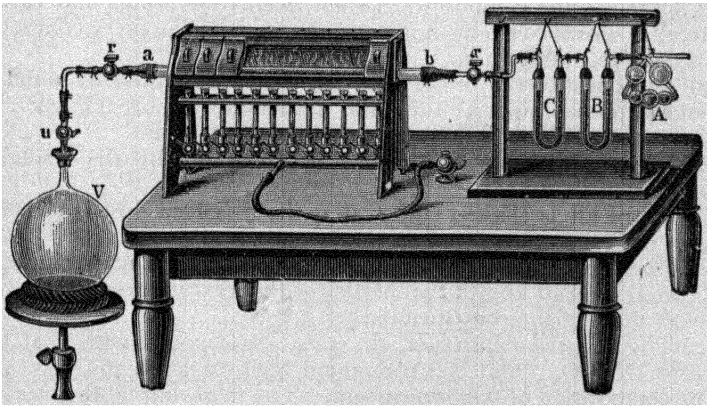


FIG. 262.—Gravimetric composition of air (Dumas and Boussingault's apparatus, modified).

and Boussingault (1841). A long tube of hard glass is packed with bright copper turnings and fitted with a stopcock at each end. It is laid in a furnace and connected at one end with a large weighed vacuous globe closed by a stopcock, and at the other with a bulb of potash solution and two U-tubes, one containing solid caustic potash and the other (next to the tube containing the copper) calcium chloride, which remove carbon dioxide and moisture from the air (Fig. 262).

The tube containing the copper is evacuated and weighed, put in the furnace, and heated to bright redness. The stopcocks are then slightly opened and air allowed to pass *slowly* over the heated copper, the oxygen being absorbed to form copper oxide and the nitrogen passing

on into the globe. When the globe is full of nitrogen the stopcocks are closed and the apparatus allowed to cool. The globe is weighed and the weight of the nitrogen it contains is found. The tube containing the copper and copper oxide is now weighed. The *nitrogen in this tube* is removed by a pump and the vacuous tube again weighed in order to find the weight of this nitrogen to be added to that in the globe The increase in weight of the *vacuous* tube gives the weight of oxygen. The nitrogen as weighed contains the argon and other inert gases. These can be determined by repeatedly passing the nitrogen over red-hot magnesium, when only the inert gases remain, the nitrogen forming magnesium nitride. Dumas and Boussingault found that 100 parts by weight of air contained 23·00 parts of oxygen and 77·00 of " nitrogen " (nitrogen + argon).

Air is a mixture, not a chemical compound.—That air is a mixture (really a solution) and not a compound of oxygen and nitrogen follows from the facts given below :

(i) Although the composition (when freed from water and carbon dioxide) is *nearly* constant, it is not quite so, whereas every compound has a definite composition.

(ii) The constituents of air may be partly separated by diffusion through a porous pipeclay tube into a vacuum (atmolysis), when the nitrogen passes through more rapidly than the oxygen.

(iii) The constituents of air may be separated by the fractional distillation of liquid air.

(iv) When air is shaken with water, the dissolved part is richer in oxygen than the undissolved part.

(v) When oxygen and nitrogen are mixed there is no evolution or absorption of heat, and the properties of the mixture are intermediate between those of the constituents

(vi) The relative density of air, 14·4, corresponds with that of a mixture $4N_2 + O_2$; that of a compound N_4O would be 36

The composition of the atmosphere.—The following table gives the average percentage composition of *dry* air by volume, at sea-level :

Dry air	100 00	Neon	0·0018
Nitrogen	78 03	Helium	0 0005
Oxygen	20·99	Krypton	0·0001
Argon	0·9323	Ozone	0·00006
Carbon dioxide	0 03	Xenon	0·000009
Hydrogen	0 01	Radium emanation	6×10^{-18}

In air there are usually present in addition to the above substances minute quantities of carbon monoxide (in towns), hydrocarbons, hydrogen peroxide, sulphur compounds such as hydrogen sulphide, sulphur dioxide and minute droplets of sulphuric acid, chlorides (especially near the sea), and dust, both inorganic and organic. The atmosphere, as Boyle said, is a " confused aggregate of effluviums " . . " there is scarcely a more heterogeneous body in the world." The average number of dust

particles per c.c. varies from about 250 in very clean sea air to about 100,000 in London air and over 2,000,000 in dusty rooms The dust particles are chiefly mineral matter, but also contain bacteria.

The probable composition of the upper layers of the atmosphere has been variously calculated According to one estimate, the composition is not very different from that at sea-level up to heights of about 20 km ; above this the proportions of hydrogen and helium rapidly increase until at 100 km. the volume percentage composition is calculated as $2{\cdot}97N_2$, $0{\cdot}11O_2$, $96{\cdot}3H_2$, 0·56He, etc , at 140 km , the hydrogen is estimated at 99 6 per cent. The upper air is also supposed to contain appreciable amounts of ozone.

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.

EXPT 4 —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. 5 —Add 6 c.c of bromine to a solution of 10 gm of caustic soda in 100 c c. of water in a flask cooled by running water. Ammonia solution is dropped in : $3NaOBr + 2NH_3 = 3NaBr + 3H_2O + N_2$. 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 convenient method for the preparation of nitrogen is the decomposition by heat of a solution of ammonium nitrite : $NH_4NO_2 = N_2 + 2H_2O$ This takes place only 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 :

$$HNO_2 + NH_3 = N_2 + 2H_2O.$$

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. In the laboratory, sodium nitrite and ammonium chloride solutions are mixed and heated.

EXPT. 6 —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. Make 5 c.c. of the solution mixed with 20 c c. of water faintly alkaline with a drop of ammonia, and make 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.

Pure nitrogen is produced by passing a mixture of nitric oxide and ammonia gas over red-hot copper :

$$6NO + 4NH_3 = 5N_2 + 6H_2O.$$

EXPT 7.—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 $(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$

Very pure nitrogen is evolved on heating sodium azide, NaN_3, or barium azide, $Ba(N_3)_2$.

Nitrogen is produced by the action of chlorine (or bromine) on a solution of ammonia

$$2NH_3 + 3Cl_2 = 6HCl + N_2 ;$$
$$HCl + NH_3 = NH_4Cl.$$

The very explosive **nitrogen trichloride** is formed as an oily liquid by the *prolonged* action of chlorine on ammonia $NH_3 + 3Cl_2 = NCl_3 + 3HCl$.

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 Its critical temperature is $-147{\cdot}13°$; the critical pressure is 33·49 atm. The liquid is colourless, b. pt. $-195{\cdot}81°$, sp gr at b pt. 0·8042. On rapid evaporation under reduced pressure it forms an ice-like solid, m. pt. $-210{\cdot}5°$/86 mm. The normal density of the pure gas is 1·2507 gm./lit. ; atmospheric nitrogen is 0·48 per cent. heavier.

Nitrogen is an inert element, since the heat of dissociation of the molecule is very large (p. 349), but it combines directly on heating 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 redness. By the action of water, nitrides 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. 8.—Heat with a blowpipe flame 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 with a condenser in circuit (Fig. 263) The gas travelling beyond the portion of the tube in which the discharge occurs glows with a yellow light. White phosphorus is converted into red phosphorus, and sodium and mercury form compounds at 150° when exposed to the gas. Nitric oxide is decomposed into nitrogen and oxygen Active nitrogen was discovered by Lord Rayleigh in 1911. Later experiments indicated that a trace of oxygen, mercury vapour, etc , is necessary in the production of active nitrogen, although an excess destroys it It is without action on hydrogen, but with acetylene yields hydrocyanic acid.

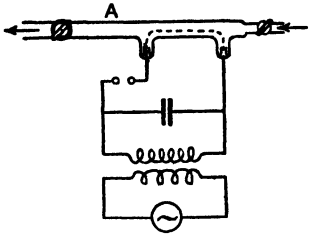


FIG 263.—Production of active nitrogen

The activity is not due to ionised nitrogen, since the glow persists when charged particles are removed from the gas. Lord Rayleigh supposed that active nitrogen is atomic nitrogen Glowing nitrogen probably contains several varieties of the element, including the normal atom and atoms and molecules with various additional amounts of energy as compared with the normal unexcited states The chemical activity seems to be due to the atomic forms, and the production of the glow to involve collisions between various types of atoms and molecules The effect of traces of impurities (optimum about 0·1 per cent.) in the production of the glow is attributed to their adsorption on the walls of the vessel, thus preventing recombination of nitrogen atoms by collision with the surface (see Strutt, *J. Chem. Soc* , 1918 , and Willey, etc., *ib.* from 1926).

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 (**buxylene**), are known only in organic derivatives. Compounds N_4H_4 and N_5H_5 exist as salts of hydrazoic acid with ammonia and hydrazine, respectively.

Ammonia and hydrazine are *basic substances*, combining with acids to form ammonium and hydrazine salts ; *e.g.*, NH_3,HCl or NH_4Cl ; N_2H_4,HCl or N_2H_5Cl, and N_2H_4,2HCl 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 ;**
$N(OH)_3$, **orthonitrous acid,** the *hypothetical* ortho-acid corresponding with ordinary nitrous acid, HNO_2.

Ammonia.—Ammonium chloride, NH_4Cl, called *sal ammoniacum* or *sal armoniacum*, appears to have been derived from the volcanoes of Central Asia, or prepared in Egypt from the soot formed on burning camels' dung. Its name was previously given to a salt prepared in the Libyan Desert near the ruins of the temple of Ammon (*cf.* Greek *ammos* = sand).

A solution of ammonium carbonate, $(NH_4)_2CO_3$, 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., was known as *spirit of hartshorn, sal volatile,* or the *volatile alkali* By distilling this with quicklime a *caustic volatile alkali*, NH_4OH, was obtained, described in Kunckel's posthumous works (1716) Gaseous ammonia was 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 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).

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 *soffioni* 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), in rock salt, in the soil, and in natural waters (as nitrite and nitrate). Ammonia is evolved on heating organic matter containing nitrogen (horn, bones, etc.) with *soda-lime*, prepared by slaking quicklime with caustic soda solution and heating till dry.

Ammonia is formed from its elements when these are sparked together : $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (Regnault, 1840) ; Deville (1864) 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

EXPT. 9.—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 on the technical scale in the **Haber process** (1905) for the synthetic production of ammonia. Since a diminution of volume occurs in the reaction: $N_2 + 3H_2 = 2NH_3$, the amount of ammonia formed in equilibrium will increase with the pressure. Heat is evolved in the reaction, hence the amount of ammonia in the equilibrium state will diminish with rise of temperature.

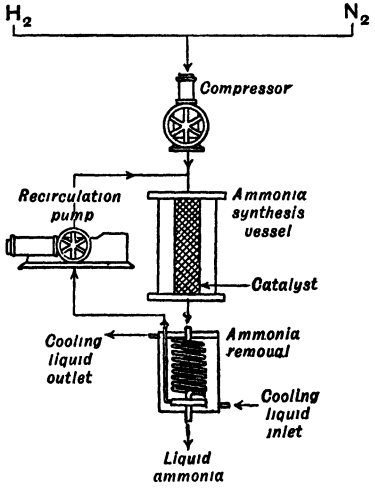


FIG. 264.—Synthetic ammonia apparatus (diagrammatic)

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., or even 1000 atm. pressure in Claude's process, over a heated catalyst (500°), which may be iron, sometimes with "promoters," *e g*, molybdenum, or silica and potassium oxide. 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:

	10	100	300	1000 atm pressure
400° C.	3·85	25	47	80
450	2·1	16·5	36	70
500	1·2	10·6	26·4	57·5
550	0·76	6·8	19	41
600	0·5	4·5	14	31·5
700	0·23	2·2	7·3	13

The cyanamide process.—Another process used for the production of ammonia from atmospheric nitrogen is the cyanamide process of Rothe, or Frank and Caro (1899). Nitrogen is passed over crushed

calcium carbide, heated at 1100° by carbon rods heated electrically inside drums of carbide, or by raking the mixture with some calcium chloride or fluoride continuously through a furnace heated with electric arcs. **Calcium cyanamide** mixed with graphite is formed as a dark grey mass called "cyanamide" or "nitrolim": $CaC_2 + N_2 = CaCN_2 + C$. This substance is a derivative of cyanamide, the amide of cyanic acid, *i.e.*, cyanic acid in which hydroxyl is replaced by the amino-group:

$$\underset{\text{Cyanic acid}}{OHCN} \rightarrow \underset{\text{Cyanamide}}{NH_2 \cdot CN} \rightarrow \underset{\text{Calcium cyanamide}}{CaN \cdot CN}$$

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 heated in a still with steam to drive out the gas:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

Preparation of ammonia in the laboratory.—In the laboratory ammonia gas is prepared by heating ammonium chloride with dry slaked lime:

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

EXPT. 10.—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, heat the flask on wire gauze, and collect the gas by upward displacement (Fig. 265). The jar is full when a piece of moist red litmus paper held near the mouth is turned strongly blue. 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. When very pure it is not absorbed by pure phosphorus pentoxide.

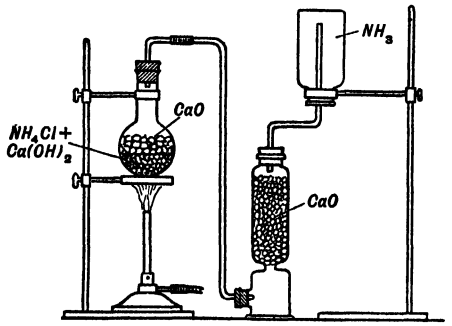


FIG. 265.—Preparation of ammonia gas.

Ammonia is 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 solution of caustic soda $(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O + 2NH_3$, or when ammonium chloride is heated with litharge an oxychloride of lead, $PbCl_2.7PbO$, used as a pigment under the name of *Cassel Yellow*, remains: $PbO + 2NH_4Cl = PbCl_2 + 2NH_3 + H_2O$

EXPT. 11.—A convenient method is to warm the concentrated aqueous solution (*liquor ammoniae fortis*, sp gr. 0·88), in a flask; the gas is dried with quicklime or lumps of caustic soda.

Ammonia is formed by the reduction of oxygen compounds of nitrogen. Thus, if a mixture of hydrogen and nitric oxide or a higher oxide of nitrogen, or even nitric acid vapour, is passed over heated 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 aluminium, 50 parts of copper, and 5 parts of zinc. This method is used for the estimation of nitrates or nitrites, the ammonia being distilled into standard acid.

EXPT. 12.—Dissolve 10 gm. of sodium nitrite and 10 gm. of caustic soda in 100 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.

Properties of ammonia.—Ammonia is a colourless gas, lighter than air, normal density 0·7708 gm./lit. (0·7717; Moles, 1930), easily liquefied by cold or pressure, forming a colourless liquid, b. pt. −33·4°, freezing to an ice-like solid, m.-pt. −77·7°. The critical temperature is 132·5°, and the critical pressure 112·30 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 (*anhydrous ammonia*). The gas has a characteristic pungent smell, and is readily soluble in water. The solution is alkaline.

EXPT. 13.—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. 17, p 193: the water rushes in as a fountain, and the litmus is turned blue (FIG. 103)

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, since a considerable amount of heat is evolved. The liquid also expands considerably.

Specific gravities $D_{15^\circ}^{15^\circ}$ of aqueous ammonia at 15·5°.

Sp gr	$\%NH_3$	Sp gr	$\%NH_3$
0·875	36·90	0 950	12·74
0·880	35 20	0·960	9 95
0 890	31 85	0 970	7 27
0 900	28·50	0·980	4 73
0 910	25 15	0 990	2 31
0·920	21·85	0 992	1 84
0·930	18 69	0·996	0 91
0·940	15 65	0·998	0·45

The aqueous solution is alkaline: $NH_3 + H^+ + OH' = NH_4^+ + OH'$. By strong cooling, the crystalline hydrates NH_3,H_2O, m pt. −79·0°, and $2NH_3,H_2O$, m pt. −78·9°, are obtained. A crystalline compound, NH_3,H_2O_2, is formed by the action of ammonia on cold concentrated hydrogen peroxide.

It has been supposed that ammonia solutions contain ammonium hydroxide, NH_4OH, a weak base of the same strength as acetic acid (p 259), together with free NH_3 $NH_4OH \rightleftharpoons NH_4^+ + OH'$ The weakness of NH_4OH (also of amines) may be due to removal of OH ions, by the lone pair of electrons on the oxygen forming a covalent link with the hydrogen attached to nitrogen

$$[R_3NH]^+ + OH^- = R_3NH \leftarrow OH \quad (R = Me, Et, \text{etc})$$

The quaternary ammonium hydroxides, with no H attached to N, cannot form such covalent compounds and are powerful bases.

$$[R_4N]^+ + OH^-$$

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.

The evaporation of liquid ammonia (not the solution) in steel pipes is used in refrigeration The gas produced is again liquefied by compression in 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. 15.—Pass ammonia, dried over quicklime or caustic soda, 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 in air 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 : $2NH_3 = N_2 + 3H_2$ It burns in oxygen with a greenish-yellow flame : $4NH_3 + 3O_2 = 6H_2O + 2N_2$, and a mixture of ammonia and oxygen explodes when ignited.

EXPT 16 —Pass a current of ammonia through a tube surrounded by a wider tube through which oxygen gas is passing (Fig 266). If a taper is held over the tubes, the ammonia burns with a large, three-coned, yellowish flame

EXPT. 17 —Prepare a mixture of oxygen and ammonia gas in the proportions $4NH_3 + 3O_2$, over mercury in a glass tube, 8 in long and 1 in diameter, sealed at one end , ignite the mixture with a taper It burns with a violent explosion

In contact with heated platinum, a mixture of ammonia gas and oxygen is catalytically oxidised to nitric oxide.

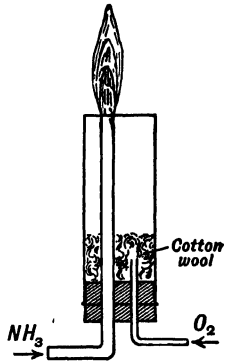


FIG 266 —Combustion of ammonia in oxygen.

EXPT 18 —Pass oxygen through a little concentrated ammonia warmed in a 200 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 oxides of nitrogen and white fumes of ammonium nitrate are formed

$$4NH_3 + 5O_2 = 4NO + 6H_2O,$$
$$2NO + O_2 = 2NO_2,$$
$$4NO_2 + O_2 + 2H_2O + 4NH_3 = 4NH_4NO_3$$

A jet of oxygen can be made to burn under the surface of the ammonia solution.

According to Schlumberger and Piotrowski (1914) mixtures with air containing 16·5 to 26·8 per cent. ammonia, can be exploded by an electric spark in a spherical glass vessel Berl and Bausch (1929) found that only the mixture with 21·9 per cent. ammonia ($4NH_3 + 3O_2$) can be exploded by a heated silver wire in a metal container at atmospheric pressure · at higher pressures, mixtures on both sides of this composition are explosive.

Mixtures of ammonia with electrolytic gas ($2H_2+O_2$) become explosive when the volume ratio of this to ammonia is slightly greater than 1, when 79 per cent. of the ammonia is decomposed on ignition. When the ratio exceeds 3, the ammonia is completely decomposed, the gaseous product containing only nitrogen, hydrogen and steam Explosion of ammonia with a deficiency of oxygen, so that the steam remains gaseous, causes complete decomposition of the ammonia, oxides of nitrogen being formed only if the ratio of NH_3 to O_2 is less than 1·6. With the ratio 1·22 the oxidation of nitrogen is a maximum (16 per cent). When oxides of nitrogen are formed, the colour of the flame changes from yellow to green, violet and white, and the proportion of nitrogen oxidised is greater than with a corresponding mixture of nitrogen, hydrogen and oxygen (Partington and Prince, 1924)

When ammonia is exploded with a mixture of carbon monoxide and oxygen ($2CO+O_2$), a practically constant fraction (95·3 per cent.) is decomposed with all ignitible mixtures (Beeson and Partington, 1925).

Ammonia gas may be detected (1) by its smell, (2) by the blueing of moist red litmus paper, (3) by the white fumes of ammonium chloride formed around a glass rod dipped in concentrated hydrochloric acid, (4) by blackening a piece of paper dipped in mercurous nitrate solution.

Ammonia reduces many heated oxides of metals (*e.g.* CuO, PbO):

$$6PbO+4NH_3=6Pb+2N_2+6H_2O.$$

With copper oxide, some nitric oxide is also formed.

Ammonia is readily absorbed by dry silver chloride, forming the compounds $AgCl,3NH_3$ and $2AgCl,3NH_3$. If the compound is sealed up in one limb of a bent tube (Fig. 102) 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. It is decomposed by ultra-violet light and by radium emanation.

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 (a little ammonia remains undecomposed; see page 546). If oxygen is now added and a spark passed, or if the mixture is passed over palladium at 200°, water is formed and two-thirds of the contraction is equal to the volume of the hydrogen. *E.g.*,

Volume of ammonia taken	= 20.
Volume of gas after sparking	= 40.
Volume after addition of oxygen	= 157·5.
Volume after explosion	= 112·5.

$\therefore$ contraction on explosion with oxygen = 45 $\therefore$ volume of hydrogen = $\frac{2}{3}\times 45=30$ $\therefore$ volume of nitrogen = 40 − 30 = 10. 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.

The volumetric composition of ammonia may be demonstrated by the following experiment.

EXPT. 19.—A long tube (FIG. 267) is divided below the stopcock into three equal volumes by rubber bands, and is filled with chlorine The tube above the stopcock is one-third filled with concentrated ammonia solution, which is added drop by drop to the chlorine, the tube being cooled by water Each drop reacts with a yellowish-green flame, and the formation of white clouds of ammonium chloride. $2NH_3 + 3Cl_2 = 6HCl + N_2$, $HCl + NH_3 = NH_4Cl$. The fumes are washed down by shaking, and 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 water, the whole being filled with water. On opening the tap water rushes into the long 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

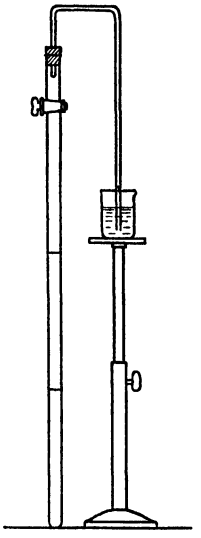


FIG 267.—Volumetric composition of ammonia (Hofmann)

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, followed by red-hot copper to reduce oxides of nitrogen, in a hard glass tube. The water formed is collected in weighed calcium chloride tubes. The nitrogen passing on is collected in a weighed exhausted globe (p. 541). In this way the ratio N : H is found to be 14 : 3. This, taken in conjunction with the density of ammonia, 8·5, corresponding with the molecular weight 17, and the volume ratio, gives the formula NH_3.

The composition of ammonia cannot be determined by exploding with oxygen, since part of the nitrogen (up to 16%) is also oxidised.

By-product ammonia.—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 carbonisation, mainly in the form of ammonia although a little hydrocyanic acid, HCN, is present. The ammonia combines with hydrogen sulphide, 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.

Ammoniacal liquor contains tar and organic compounds, free ammonia, 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:

$$NH_4HS \rightleftharpoons NH_3 + H_2S\ ;$$
$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

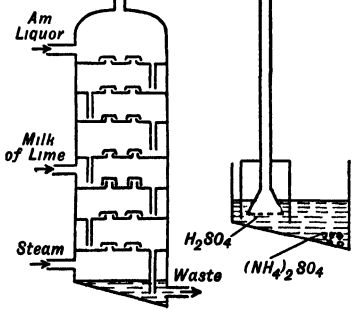


FIG. 268.—Ammonia still.

A typical still is shown in Fig 268. It consists of an iron column containing perforated plates. In the upper part the ammoniacal liquor is treated with steam passed in at the base, and ascending through the tower to drive out the volatile ammonia; most of the steam is condensed in the upper part. Milk of lime is added in the middle part, and the sludge allowed to pass out at the base. The ammonia set free by the lime is driven out by steam.

The ammonia is bubbled through 60 per cent. sulphuric acid in a lead-lined tank, 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 ammonia gas is passed through a washer containing milk of lime to remove hydrogen sulphide, 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 0·88 (35 per cent NH_3) requires very careful cooling in its preparation The ammonium sulphate is nearly all used in agriculture as a fertiliser

Attempts have been made to recover ammonia from crude coal gas by passing it through sulphuric acid without previous deposition of ammoniacal liquor. This direct process is worked in connection with coke-ovens.

Hydroxylamine. — Hydroxy-ammonia, or hydroxylamine, NH_2OH, was discovered by Lossen in 1865. Its salts are obtained by.

1. The reduction of nitric oxide, NO, with nascent hydrogen·

$$NO + 3H = NH_2OH.$$

A stream of nitric oxide is passed through a series of flasks containing granulated tin and concentrated hydrochloric acid. Reduction occurs, with the formation of **hydroxylamine hydrochloride,** NH_2OH,HCl [or **hydroxylammonium chloride,** $NH_3(OH)Cl$] and ammonium chloride, NH_4Cl. According to Divers, an ammonium salt is not formed in the complete absence of air. The solution is treated with hydrogen sulphide to precipitate tin as sulphides, filtered, and evaporated to dryness. The residue is extracted first with cold, then with boiling absolute alcohol, which dissolves the hydroxylamine but not the ammonium salt Hydroxylamine hydrochloride is then precipitated from the alcoholic solution by ether.

2. The reduction of ethyl nitrate, $C_2H_5NO_3$, by nascent hydrogen:

$$C_2H_5NO_3 + 6H = C_2H_5OH + NH_2OH + H_2O.$$

Thirty gm. of $C_2H_5NO_3$, 120 gm. of granulated tin, and 40 gm. of HCl (sp gr. 1·12) are mixed, when reaction occurs spontaneously. The solution is treated as in (1).

3. The electrolytic reduction of nitric acid (Tafel, 1902):

$$HNO_3 + 6H = NH_2OH + 2H_2O.$$

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,** $(NH_2OH)_2,H_2SO_4$, is formed.

4. The interaction of nitrites and sulphites in solution (Raschig, 1887):

$$NaNO_2 + NaOH + 2SO_2 + 2H_2O = NH_2OH,H_2SO_4 + Na_2SO_4.$$

The reaction occurs in three stages, as follows:

(*a*) $NaNO_2 + 3NaHSO_3 = HO{\cdot}N(SO_3Na)_2 + Na_2SO_3 + H_2O$.
(*b*) $HO{\cdot}N(SO_3Na)_2 + H_2O = HO{\cdot}NH(SO_3Na) + NaHSO_4$.
(*c*) $HO{\cdot}NH(SO_3Na) + H_2O = HO{\cdot}NH_2 + NaHSO_4$.

EXPT. 20.—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**, $(NH_2OH)_2.H_2SO_4$. 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.

By these methods salts of hydroxylamine are produced: if caustic alkali is added to a solution of a salt, free hydroxylamine is first formed, but is unstable.

Anhydrous hydroxylamine, NH_2OH, 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: $2CH_3OH + 2Na = 2CH_3ONa + H_2$), filtering off the sodium chloride, and distilling under reduced pressure (40 mm.): $CH_3ONa + NH_2OH,HCl = CH_3OH + NaCl + NH_2OH$. Crismer (1891) distilled the double compound $ZnCl_2.2NH_2OH$ (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 low pressure (13 mm.): $(NH_4O)_3PO_4 = H_3PO_4 + 3NH_2O$.

Properties of hydroxylamine.—Pure hydroxylamine forms colourless, very deliquescent, odourless crystals, sp. gr. 1·35, m. pt. 33°. 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 basic and precipitates many metals (Zn, Al) as hydroxides. Hydroxylamine is a weaker base than ammonia, and its salts are hydrolysed in solution.

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:

$$2NH_2O + 4CuO = N_2O + 3H_2O + 2Cu_2O;$$
$$4FeCl_2 + 2NH_2O = N_2O + 4FeCl_2 + 4HCl + H_2O.$$

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 :

$$\underset{\text{Nitrous acid}}{HO{\cdot}NH_2} + \underset{\text{Hyponitrous acid}}{ON{\cdot}OH} = HO{\cdot}N{:}N{\cdot}OH + H_2O = N_2O + 2H_2O.$$

In absence of water, hydroxylamine can act as a very feeble acid : with lime it gives $HOCa{\cdot}O{\cdot}NH_2$, and with calcium $(H_2NO)_2Ca$, both explosive on heating. Fulminic acid, C:N·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 red colour appears on heating (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 three fingers in the research. Dulong did not publish his work ; an abstract of it by Thenard and Berthollet appeared later. In the meantime Davy (1813) obtained the compound by the same method, 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 :

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl;$$

$$NH_3 + 3HOCl = NCl_3 + 3H_2O.$$

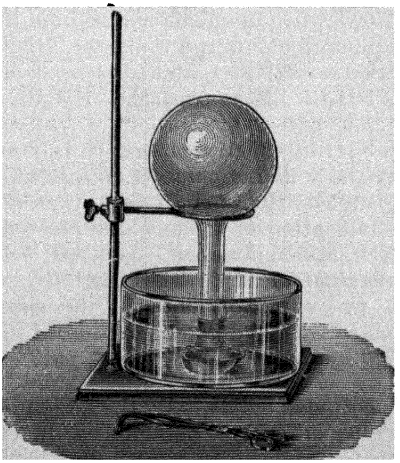


FIG. 269.—Preparation of nitrogen trichloride.

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. 269). 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 by a long pipette into

the flask, covered with a strong box, 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.

Nitrogen trichloride detonates with great violence at 100°, the sp gr of the liquid is 1 65, it freezes below −40° (Davy). It also explodes in contact with phosphorus, many oils (including turpentine), fused caustic potash, phosphine, rubber, and nitric oxide

Gattermann found that the oil 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.

Monochloramine, NH_2Cl, is formed as unstable colourless crystals, m. pt. −66°, when ammonia and sodium hypochlorite are mixed in solution in equimolecular proportions, the liquid is distilled in a vacuum, the vapour dried with K_2CO_3 and condensed in liquid air $NaOCl + NH_3 = NaOH + NH_2Cl$. **Monobromamine,** NH_2Br, is formed by the action of ammonia gas on a solution of bromine in ether· $2NH_3 + Br_2 = NH_2Br + NH_4Br$ **Dichloramine,** $NHCl_2$, is obtained in solution (Chapin, 1929) by the action of chlorine on a solution of ammonium sulphate buffered to an acidity of *p*H 4·5 to 5, when it is the sole product, and also by the acidification of monochloramine solution By the action of NCl_3 on KBr, Millon obtained a dark red, volatile, explosive oil, possibly **nitrogen tribromide. Nitrogen trifluoride,** NF_3, is a colourless, rather inert, gas, b. pt. −119°, obtained by the electrolysis of fused NH_4HF_2; when mixed with hydrogen and kindled it explodes violently, giving nitrogen and hydrogen fluoride (Ruff, 1928)

Nitrogen iodide.—By the action of iodine on a solution of ammonia, Courtois (1812) obtained a black explosive powder. This was examined by Gay-Lussac and by Davy (1814), who showed that it contained nitrogen and iodine; Gladstone (1851–54) gave it the formula NHI_2, whilst Gay-Lussac, and 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, reacting with more ammonia to form iodide of nitrogen, possibly by decomposition of ammonium hypoiodite:

(*a*) $NH_4OH + I_2 = NH_4I + HOI$;
(*b*) $NH_3 + HOI = NH_4OI$,
(*c*) $3NH_4OI \rightleftharpoons N_2H_3I_3 + NH_4OH + 2H_2O$.

Iodide of nitrogen is decomposed by sodium sulphite:

$$N_2H_3I_3 + 3Na_2SO_3 + 3H_2O = 3Na_2SO_4 + 2NH_4I + HI.$$

The free acid may be titrated with baryta and the iodide with silver nitrate, and so the composition 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. 21 —If a solution of iodine in KI 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 22 —Triturate gently 1 gm of iodine with concentrated ammonia A black powder is formed, which is filtered off, and 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 stick, it explodes—sometimes spontaneous explosion occurs. If two portions are close together and one is exploded, the shock brings about the explosion of the other portion. Violet fumes of iodine are evolved

Nitrogen iodide is an active oxidising agent, oxidising sulphites to sulphates, arsenious acid to arsenic acid, etc. Each atom of iodine has an oxidising effect of an atom of oxygen, as in hypoiodous acid, HOI.

Nitrogen tri-iode, NI_3, is obtained by the action of gaseous ammonia on $KIBr_2$, and remains as a black residue on quickly washing with water

$$KIBr_2 \rightleftharpoons KBr + IBr, \quad 3IBr + 4NH_3 = NI_3 + 3NH_4Br.$$

Hydrazine.—Hydrazine or diamide, N_2H_4, prepared by Curtius in 1887 from organic compounds, was obtained by Raschig in 1907 by the action of sodium hypochlorite on ammonia solution in the presence

of a little glue. Monochloroamine is first formed and then reacts with ammonia to form hydrazine :

$$NH_3 + NaOCl = NH_2Cl + NaOH;$$
$$NH_3 + NH_2Cl = NH_2{\cdot}NH_2 + HCl.$$

EXPT. 23.—To 200 c c. of 20 per cent. ammonia add 5 c c of 1 per cent. solution of glue and 100 c c of freshly made NaOCl solution (obtained by saturating cold 5 per cent NaOH solution with chlorine). Heat rapidly to boiling and keep at the boiling point for half an hour Cool and acidify with dilute sulphuric acid The hydrazine sulphate, N_2H_4,H_2SO_4 (6 gm) crystallises out and is filtered in a Buchner funnel.

Hydrazine is formed in small quantities by the reduction of **potassium nitrososulphate,** obtained by saturing an alkaline solution of potassium sulphite with nitric oxide This salt (Davy, 1800), with the empirical formula $K_2SO_3{\cdot}N_2O_2$, is suspended in ice-cold water and treated with sodium amalgam ·

$$K_2SO_3{\cdot}N_2O_2 + 6H = K_2SO_4 + H_2O + N_2H_4.$$

Potassium nitrososulphate is best prepared by passing nitric oxide through a series of flasks containing concentrated alkaline potassium sulphite solution, the gas being led over the surface of the solution, and the air being first displaced by hydrogen. The salt crystallises out.

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°/26mm., is obtained This is called **hydrazine hydrate,** but appears to be a solution of maximum boiling point. The solution of the hydrate may be concentrated to 95 per cent. by distilling it with xylene, which carries over the water. 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.

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 : $3N_2H_4 = N_2 + 4NH_3$. By the action of sodium on anhydrous hydrazine in absence of oxygen, a crystalline solid, $H_2N{\cdot}NHNa$, is obtained, which explodes violently in presence of oxygen or moisture.

Hydrazine in solution acts as a very weak base : it forms two series of salts, *e g.*, N_2H_4,HCl and $N_2H_4,2HCl$; $2N_2H_4,H_2SO_4$ and N_2H_4,H_2SO_4. The ordinary **hydrazine sulphate** is N_2H_4,H_2SO_4,

perhaps $N_2H_5 \cdot HSO_4$. The salts are ionised and hydrolysed in solution:

$$N_2H_4,2HX \rightleftharpoons N_2H_4,HX + HX \rightleftharpoons N_2H_5 + H' + 2X'.$$

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: $3N_2H_4 + 2H_2SO_4 + 2KIO_3 = 2HI + 2KHSO_4 + 6H_2O + 3N_2$. 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.—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. $3N_2H_4 + 5O = 2HN_3 + 5H_2O$

EXPT. 24.—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). **Lead azide**, $Pb(N_3)_2$, is used as a detonator in place of mercury fulminate.

Hydrazoic acid is also formed by the decomposition of hydrazine nitrite under special conditions (*cf.* $NH_3,HNO_2 = N_2 + 2H_2O$).

$$N_2H_4,HNO_2 = HN_3 + 2H_2O.$$

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. Sodium azide is produced by fusing sodamide with sodium nitrate:

$$3NaNH_2 + NaNO_3 = NaN_3 + 3NaOH + NH_3.$$

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 at 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 at 190°. The sodamide swells up and ammonia is evolved:

$$NaNH_2 + N_2O = NaN_3 + H_2O;$$
$$NaNH_2 + H_2O = NaOH + NH_3.$$

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 poisonous and 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 thiocyanate but discharged by hydrochloric acid, 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 (*i.e.*, N_4H_4) and $N_2H_5N_3$ (*i e.*, N_5H_5) are obtained in colourless explosive crystals.

The vapour density corresponds with HN_3, the constitutional formula may be written H—N<N‖N Thiele represented it as N N.NH, which agrees with the formation of NH_3 and N_2H_4 on reduction, but later returned to the older formula The group N_3 is a *negative group*, whilst NH_2 is a *positive group*, H—NH_2 is a base

Chlorazide, N_3Cl, is a colourless very explosive gas obtained by the action of sodium hypochlorite and boric acid on sodium azide **Iodazide**, N_3I, is a pale yellow explosive solid obtained by the action of iodine on silver azide

Thiele's formula for hydrazoic acid may be written $\overset{\times\times}{N}\overset{\times}{\cdot}.N:.\dot{N}\overset{\cdot}{\circ}H$ or $N \overleftarrow{-} N=NH$. There is a great similarity of the formulae of the azide ion, the cyanate ion, and the neutral nitrous oxide molecule:

$$[\dot{N}::N::N]' \qquad [\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}\cdot\cdot C:\underset{\cdot}{O}]' \qquad N\cdot\cdot N\cdot\cdot \underset{\cdot\cdot}{O}$$

The linear structure of the azide ion in crystals is firmly established by X-ray analysis. The electronic formulae of the nitrogen and carbon monoxide molecules, and of the cyanide ion, are also very similar:

$$:N:::N: \qquad \overset{\times}{\underset{\times}{C}}::O: \qquad [\overset{\times}{\underset{\times}{C}}::N.]'$$
$$N\equiv N \qquad C\leftrightharpoons O \qquad C\leftrightharpoons N$$

In the last case, an extra electron must be introduced to complete the group of six on the N atom, thus producing a univalent anion.

CHAPTER XXX

THE OXIDES AND OXY-ACIDS OF NITROGEN

Oxides and oxy-acids of nitrogen.—The following table of oxides and oxy-acids of nitrogen may be compared with that of the oxy-compounds of chlorine (p. 329).

Nitrous oxide, N_2O	→	**Hyponitrous acid** $HO{\cdot}N{\cdot}N{\cdot}OH$ / Isomeric **nitramide** $NO_2{\cdot}NH_2$
Nitric oxide, NO	→	**Nitrohydroxylamic acid**, $HON\,NO_2H$
Nitrogen trioxide, or **Nitrous anhydride**, N_2O_3	→	**Nitrous acid**, HNO_2
Nitrogen dioxide (tetroxide), NO_2 or N_2O_4	↗↘	
Nitrogen pentoxide, or **nitric anhydride**, N_2O_5	→	**Nitric acid**, HNO_3
Nitrogen hexoxide, N_2O_6 (?)	→	**Pernitric acid**, HNO_4 (?)

The union of nitrogen and oxygen.—Nitrogen and oxygen combine directly at high temperatures to form colourless **nitric oxide**: $N_2 + O_2 \rightleftharpoons 2NO$. With excess of oxygen this forms on cooling red **nitrogen dioxide**: $2NO + O_2 = 2NO_2$. Nitrogen dioxide dissolves in water, 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 gaseous nitrogen dioxide and nitric oxide: $N_2O_3 \rightleftharpoons NO_2 + NO$.

The nitric oxide is again oxidised if excess of oxygen is present, and finally all the oxides of nitrogen are converted into dilute nitric acid.

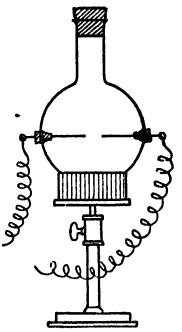


FIG. 270.—Combination of nitrogen and oxygen by sparking

EXPT 1.—Pass a series of sparks through dry air in a globe (Fig. 270). After a time this becomes yellowish in colour, and if shaken with litmus solution the latter is turned red. This observation is due to Priestley (1779).

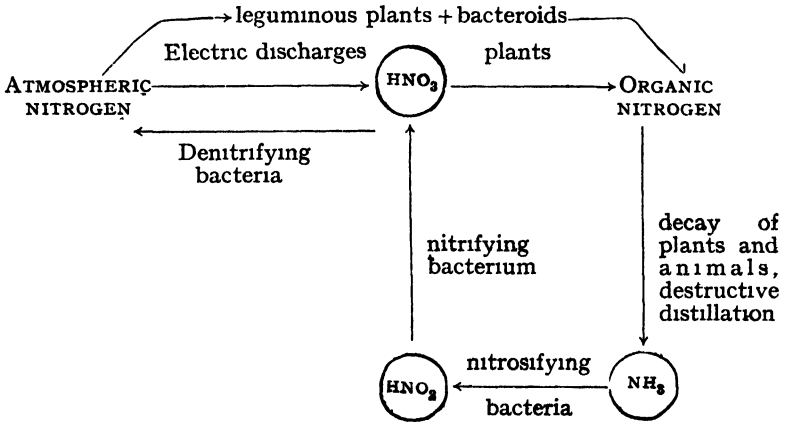
Nitric acid is also formed when a mixture of detonating gas (2 vols. of H_2 + 1 vol. of O_2) with air is exploded by a spark. If the volume of air is more than double that of the detonating gas, the temperature of explosion is too low to lead to the formation of nitric acid. Thus, no acid is formed on exploding a mixture of hydrogen and air. This observation is due to Cavendish (1781).

The nitrogen cycle.—Nitric acid is formed by electrical discharges in the atmosphere, and is washed down by rain. It is estimated that 250,000 tons 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, leguminous plants can take up atmospheric nitrogen which is converted into organic nitrogen by the agency of micro-organisms which occur in nodules, called *Bacteroids*, on the root. Algae, fungi and mosses, and a bacterium, *Azotobacter Chroococcum*, present in soil, 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 **nitrosifying bacteria** to nitrites, and these by the **nitrifying bacterium** to 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** in the soil.

The nitrogen cycle in Nature may be represented diagrammatically as shown below.

NITROGEN CYCLE



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, probably from the oxidation of ammonia formed by the decomposition of organic matter in the presence of feeble alkalies, by the activity of micro-organisms present in 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 material is lixiviated and 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 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 and with calcite are deposited. The rhombic form is stable below 129°, a second rhombohedral form at higher temperatures. Nitre melts at 336°, 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** (*q v*). Potassium nitrate is used in pickling meat, to which it imparts a bright red colour (*e g*, hams), and in medicine.

Sodium nitrate; Chile nitre.—In 1809 the existence of extensive deposits of sodium nitrate, $NaNO_3$, was discovered in the rainless districts of Chile. In the surveyed area the supply is estimated as 240,000,000 tons. The export from Chile began in 1830; in recent years it averaged about 2,500,000 tons per annum

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 potassium nitrate, and of nitric acid for the manufacture of explosives, dyes and drugs.

Sodium nitrate crystallises in rhombohedra resembling cubes, isomorphous with calcite, hence it is sometimes called "cubic nitre." It differs from potassium nitrate in being deliquescent, 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 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 about 1150 A.D., if not earlier, for the production of fireworks *Greek fire*, used in the Byzantine period, was a mixture of salt, resin, quicklime, pitch, and sulphur, although some kinds may have contained saltpetre. The invention of gunpowder in the West is usually credited to Roger Bacon (1214–1292), who in his *de secretis operibus artis et de nullitate magiae*, probably composed about 1248, definitely mentions saltpetre and sulphur as constituents, but conceals charcoal in an anagram. The full recipe is given in the *Liber Ignium* of Marcus Graecus, the earliest MSS. of which are practically contemporary with Bacon ; it 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 6 : 1 . 1, the materials being ground and incorporated under stone rollers. (Marcus Graecus gives 6 : 2 : 1.) 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) considered that the explosion of gunpowder cannot adequately be represented by a chemical equation, since the reactions are complicated.

The gaseous product consists principally of carbon dioxide, carbon monoxide and nitrogen, whilst the solid product (including that in the dense smoke) consists mainly of potassium carbonate, potassium sulphate and potassium sulphide We may, therefore, represent the principal reactions in the explosion by the equations

$$4KNO_3 + 5C = 2K_2CO_3 + 2N_2 + 3CO_2 ;$$
$$2KNO_3 + 3C = K_2CO_3 + CO_2 + CO + N_2 ;$$
$$2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2 ;$$
$$2KNO_3 + S + C = K_2SO_4 + N_2 + CO_2.$$

By the action of sulphur alone on nitre, sulphur dioxide and potassium nitrite are formed as well as potassium sulphate.

Nitric acid.—Nitric acid appears to have been known in Europe about 1100 A.D., if not earlier. Geber describes the preparation of *aqua fortis* by distilling nitre with alum and copper sulphate: "Take a pound of vitriol of Cyprus, half a pound of saltpetre, and a quarter of alum of Jameni; extract the solutive water with redness of the alembic. If you dissolve in it a fourth of salammoniac it is much sharper." Glauber, about 1658, seems to have obtained a more concentrated fuming acid by distilling nitre with oil of vitriol. The acid was therefore known as *spiritus nitri Glauberi*. The presence of oxygen in nitric acid was demonstrated by Lavoisier in 1776 by heating nitrate of mercury, which evolved oxygen Scheele (1777) showed that the vapour is decomposed by heat.

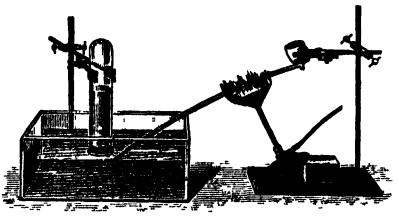


FIG. 271.—Decomposition of nitric acid by heat

EXPT. 2.—Arrange a clay tobacco pipe as shown in Fig. 271. 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.

Cavendish (1785) passed sparks through a mixture of air and oxygen confined over mercury and potash solution in an inverted **V**-tube (Fig. 272). The oxides of nitrogen were absorbed by the alkali, and the residual oxygen was then absorbed by a solution of liver of sulphur, only a very small bubble of gas remaining (probably argon; see p. 595).

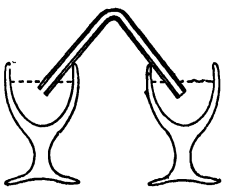


FIG. 272.—Cavendish's apparatus for sparking air over potash solution

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 actually formed in their room."

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 at 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

then usually cracks, and part of the acid is always decomposed with production of red oxides of nitrogen: $4HNO_3 \rightleftharpoons 4NO_2 + 2H_2O + O_2$. These dissolve in the acid, colouring it yellow.

EXPT. 3.—Add 49 gm. (26 c.c.) of concentrated sulphuric acid to 50 gm. of potassium nitrate in a stoppered retort, and stir with a glass rod. Heat on wire gauze, and collect the nitric acid in a cooled receiver Notice the red gas at the beginning and end of the process. The acid obtained is yellow. Add a piece of copper foil to it . the metal does not usually dissolve Add a few drops of water the copper dissolves and red oxides of nitrogen are evolved Ordinary nitric acid may be concentrated by distillation with concentrated sulphuric acid.

Pure nitric acid is obtained by redistilling on a water-bath under reduced pressure, and passing ozonised oxygen through the distillate; or by freezing 98 per cent. acid, when colourless crystals, m. pt. $-41{\cdot}3°$, separate. It is a colourless liquid of sp. gr. 1·52

The liquid acid and the vapour are slightly dissociated at the ordinary temperature: $2HNO_3 \rightleftharpoons N_2O_5 + H_2O$, 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. Nitric acid decomposes on distillation under atmospheric pressure.

It begins to boil at 78·2°, with decomposition When three-fourths of the acid have 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. $-18{\cdot}5°$), are known.

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 **fuming nitric acid**, containing oxides of nitrogen and used as an oxidising agent, is prepared by distilling nitre and sulphuric acid with a little starch, which reduces a portion of the nitric acid to N_2O_3 and N_2O_4.

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 at 15° of mixtures of nitric acid and water 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, largely ionised in solution: $HNO_3 \rightleftharpoons H^{\cdot} + NO_3'$, is monobasic and forms salts, the nitrates, which are obtained by the action of nitric acid on the metals (when oxides of nitrogen, not hydrogen, are usually evolved), on the oxides or hydroxides, or on the carbonates. Acid nitrates, *e g.*, NH_4NO_3,HNO_3 and $NH_4NO_3,2HNO_3$ are known.

Nitric acid also acts as an oxidising agent. Hot concentrated nitric acid oxidises iodine to iodic acid, HIO_3. Phosphorus is oxidised to phosphorous and phosphoric acids (white phosphorus may cause an explosion), sulphur is oxidised 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. 4.—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 sometimes with explosion.

Hydrogen sulphide is not oxidised by pure nitric acid, but in presence of nitrogen oxides it is decomposed with separation of sulphur (see p. 495). 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, in the cold, a black solution, from which nitric oxide is expelled on heating:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

This is utilised as a test for nitric acid and nitrates. In the case of nitrates, *concentrated* sulphuric acid must be added before the colour appears (*nitrites* give the reaction with *dilute* acid)

EXPT 5.—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) 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 and nitrates are (i) the red colour produced with a solution of brucine in concentrated sulphuric acid, (ii) the deep blue colour with a solution of diphenylamine in concentrated sulphuric acid, (iii) the evolution of red oxides of nitrogen when the substance is heated with concentrated sulphuric acid and copper turnings, (iv) *nitron* reagent (10 per cent in 5 per cent. acetic acid) forms a white crystalline precipitate of nitron nitrate, $C_{20}H_{16}N_4.HNO_3$, on adding 5 drops of reagent and 1 drop of dilute sulphuric acid to 5 c.c. of nitrate solution.

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 remaining metals form nitrates. Aluminium is scarcely attacked by cold nitric acid; iron and chromium become "passive" in the concentrated acid; lead becomes covered with a protective film of nitrate. During the reactions 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 magnesium, acting on cold dilute (1 or 2 per cent) nitric acid: $Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$.

H. E. Armstrong and Acworth (1877) suggested that the **primary reaction** in *all* cases is the liberation of nascent hydrogen:

$$\text{I} \quad M + HNO_3 = MNO_3 + H.$$

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. $3HNO_2 = HNO_3 + 2NO + H_2O$.

$\therefore$ 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, Zn, Sn, Cd, Mn, Mg (also gives H_2) The product, however, depends on the concentration and temperature of the acid (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 and nitrous oxide are evolved Sabatier and Senderens say that some hydrogen and nitrogen are evolved with zinc.

Veley (1890) 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. 6.—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 c.c. of hydrazine hydrate solution. 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 hydrazine decomposes it.

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:

I $\quad Cu + 4HNO_2 = Cu(NO_2)_2 + 2H_2O + 2NO.$

II (*a*) $Cu(NO_2)_2 + 2HNO_3 = Cu(NO_3)_2 + 2HNO_2$;

(*b*) $HNO_3 + H_2O + 2NO \rightleftharpoons 3HNO_2.$

The nitric oxide reduces nitric acid to nitrous acid, and nitric oxide is evolved only at a certain concentration of nitrous acid.

The manufacture of nitric acid.—Nitric acid is made on the large scale by the distillation of sodium nitrate with concentrated sulphuric acid: $3NaNO_3 + 2H_2SO_4 = Na_2SO_4 + NaHSO_4 + 3HNO_3$

One or two tons of previously dried sodium nitrate (Chile nitre) are heated with rather more than this weight of concentrated sulphuric

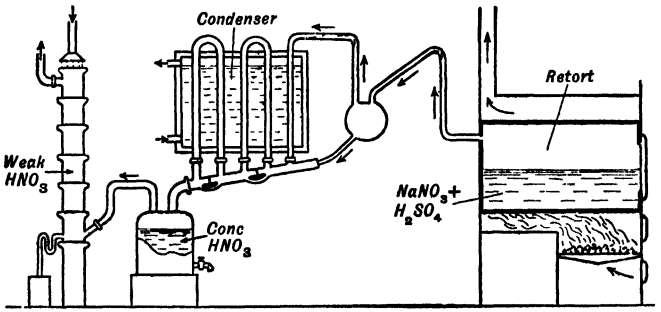


FIG 273.—Manufacture of nitric acid by distilling sodium nitrate with sulphuric acid

acid (93 per cent. H_2SO_4) in a large cast-iron pot, built in a brickwork furnace so as to allow of very uniform heating (Fig. 273). 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.

The acid is condensed in some type of cooler, consisting of vitreous silica spirals cooled in water, stoneware U-tubes or horizontal glass tubes cooled partly by air and water, S-shaped tubes of silicon iron, or large stoneware Woulfe's bottles. The red oxides of nitrogen also produced are condensed by water in a stoneware tower at the end, packed with hollow stoneware cylinders or balls.

$$4NO_2 + O_2 + 2H_2O = 4HNO_3.$$

In the **Valentiner process** (1891) the apparatus is air-tight, and a vacuum is maintained by an air-pump. The distillation under reduced pressure (25 cm.) takes place at a lower temperature (100°–150°), so that

there is less decomposition, and the reaction also occurs more rapidly than in the ordinary process.

The liquid residue in the retort is run out and allowed to solidify; it is a mixture or compound of about equimolecular proportions of $NaHSO_4$ and Na_2SO_4, 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 industry was laid by the Norwegians Birkeland and Eyde in 1902. As carried out in Norway, at Notodden and Rjukan, the process utilised 350,000 horse-power derived from water-power. Air is drawn through the lenticular cavity in a flat circular furnace (Fig. 274), in which an electric arc burning between water-cooled copper poles is spread out by an electromagnet into a disc, the temperature of which is about 3000° In 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 after rapid cooling to "freeze" the equilibrium, leave the furnace at about 1000°, containing 1 per cent of NO, 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, and then pass through large aluminium pipes exposed to the air where they cool to 50°.

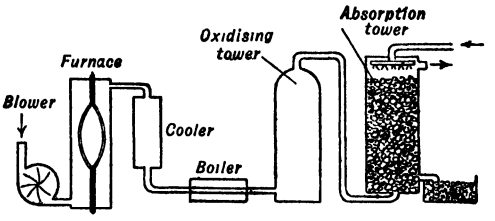


FIG 274.—Diagram of the arc process for producing nitric acid from the atmosphere

When the gas has cooled below 600°, formation of nitrogen dioxide begins: $2NO + O_2 \rightleftharpoons 2NO_2$; this is a somewhat slow process, since it is a termolecular reaction involving the collision of three molecules, and to give time for the reaction the gases pass through a large empty iron oxidising tower and then to the three or four gigantic absorption towers, 65–80 ft. high and 18 ft. diameter, built of granite slabs and packed with broken quartz over which water is circulated. In these towers formation of nitric acid occurs:

$$2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3,$$
$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

The NO is reoxidised by the excess of air present, forming NO_2, which re-enters the reaction. Nearly all the nitrous acid is so 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 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 passes into an iron tower packed with quartz, down which a solution of sodium carbonate trickles, which absorbs nearly all the residual oxides with formation chiefly of **sodium nitrite** with some nitrate

$$[NO + NO_2 \rightleftharpoons] \; N_2O_3 + 2NaOH = 2NaNO_2 + H_2O.$$

The oxidation of ammonia.—In 1788, the Rev. Isaac Milner, President 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 as a catalyst: $4NH_3 + 5O_2 = 4NO + 6H_2O$. 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.

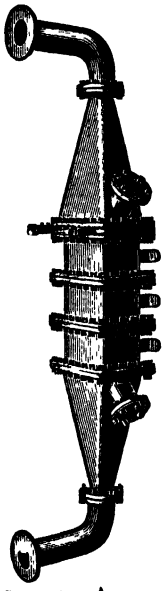


FIG 275.—Ammonia oxidation converter

Ammonia gas and also sodium azide are oxidised to nitrite by oxygen in presence of alkali · $NaN_3 = NaN + N_2$; $NaN + O_2 = NaNO_2$, $NH_3 = NH + H_2$, $NH + O_2 = HNO_2$.

EXPT. 7.—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 gas and white fumes in a globe attached to the tube

The best results are obtained when the gas passes very rapidly over the catalyst; with a slow current of gas much free nitrogen is produced. A mixture of 1 vol. of purified ammonia gas and 7·5 vols. of air filtered from dust, or the mixture $NH_3 + 2O_2$ with sufficient steam to render it non-explosive, is passed through fine platinum gauzes stretched across a rectangular aluminium box and heated electrically (Fig. 275). The gases may also be heated to about

500° before passing to the apparatus, when the reaction proceeds automatically. More than 90 per cent of the ammonia is oxidised to NO, and with air 1 sq ft of double catalyst gauze will produce 7 tons of HNO_3 per twenty-four hours.

If the cooled oxidised 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.

$$4NO_2 + O_2 + 2H_2O + 4NH_3 = 4NH_4NO_3$$

Nitric anhydride or nitrogen pentoxide.—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 also prepared by dehydrating concentrated nitric acid by phosphorus pentoxide (Weber, 1872).

$$2HNO_3 = N_2O_5 + H_2O.$$

Crystalline nitrogen pentoxide is also formed by passing ozonised oxygen through cooled liquid nitrogen tetroxide:

$$N_2O_4 + O_3 = N_2O_5 + O_2.$$

To pure concentrated nitric acid, freshly distilled over concentrated sulphuric 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 as low a temperature as possible The distillate in the cooled receiver consists of two layers: the upper orange-red layer is poured off and 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 carbon dioxide and ether.

Nitrogen pentoxide forms white very hygroscopic crystals, stable below 0° but decomposing slowly at the ordinary temperature even in sealed tubes, and becoming yellow: $2N_2O_5 = 2N_2O_4 + O_2$. They melt with decomposition at 29·5°, and form a dark brown liquid, which decomposes into red NO_2 and oxygen at 50°. 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.

Nitric oxide.—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 diluted nitric acid and called it *nitrous air*.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

EXPT. 8.—Copper turnings are placed in a flask (Fig. 276) and a mixture of equal volumes of concentrated nitric acid and water poured on. At first, the air in the flask becomes red, due to the action of the nitric oxide on atmospheric oxygen $2NO + O_2 = 2NO_2$. The gas then 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. The gas, especially in the later stages of the reaction, contains variable amounts of nitrogen and nitrous oxide. 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.

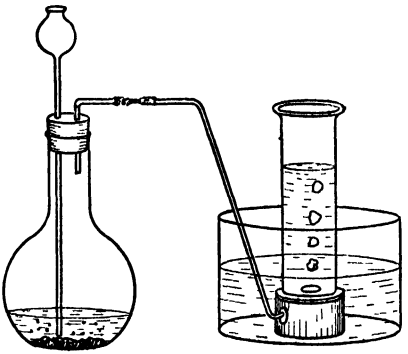


FIG. 276.—Preparation of nitric oxide.

Nearly pure nitric oxide may be obtained by heating a mixture of potassium nitrate, ferrous sulphate, and dilute sulphuric acid. A dark solution of NO in ferrous sulphate is formed, which breaks up on heating:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

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, nitric oxide is evolved:

$$3FeCl_2 + NaNO_3 + 4HCl = 3FeCl_3 + NaCl + 2H_2O + NO.$$

Perfectly pure nitric oxide is obtained (W. Crum, 1847) by shaking mercury in a flask with concentrated sulphuric acid to which nitric acid or a 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 solid substance is dissolved in the least amount of water and passed into the Lunge **nitrometer** (Fig. 277), 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.

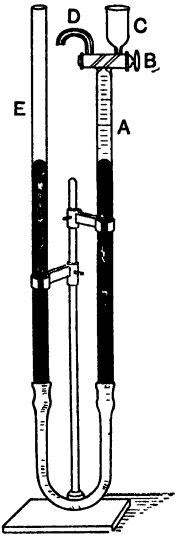


FIG. 277.—Lunge's nitrometer

Pure nitric oxide is evolved by dropping a solution of sodium nitrite and potassium ferrocyanide into dilute acetic acid:

$$FeC_6N_6'''' + NO_2' + 2H^{\cdot} = FeC_6N_6''' + NO + H_2O;$$

and by the action of sodium nitrite solution on an acidified solution of potassium iodide:

$$2HNO_2 + 2HI = 2H_2O + 2NO + I_2$$

The gas should be collected over mercury, as it acts slightly on water, evolving traces of nitrous oxide.

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. The volumes at S.T.P. absorbed by 1 vol. of water are:

Temp.	0°	15°	30°	60°
Vols of NO	0·074	0·051	0·040	0·0295

It is difficult to liquefy: the liquid, which has a somewhat darker blue colour than liquid oxygen, boils at −151·7°, and freezes at −163·6° to a solid of the same colour. The critical temperature is −96°, and the critical pressure 64 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.

Liquid or compressed nitric oxide slowly decomposes into N_2O_3 and nitrous oxide, N_2O. $4NO = N_2O_3 + N_2O$. This reaction also occurs in presence of water

Nitric oxide is slowly 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 an alkaline solution of a sulphite, forming a **nitrososulphate**, $Na_2(NO)_2SO_3$, or $NaON\ N\ O{\cdot}SO_3Na$

Nitric oxide combines with free oxygen to form red nitrogen dioxide: $2NO + O_2 = 2NO_2$ By passing nitric oxide through liquid oxygen, or by the action of air on solid nitric oxide at $-180°$, a green solid oxide, N_3O_4, is said to be formed Nitric oxide and oxygen dried with phosphorus pentoxide do not combine.

Some combustible substances burning freely in air continue to burn in 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 probably burn in the oxygen liberated by the thermal decomposition of the gas. A lighted taper, burning sulphur, charcoal, and feebly burning phosphorus are extinguished, but if burning brightly the combustion of the phosphorus continues brilliantly, a red gas 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, formed by shaking a few c c of carbon disulphide in a jar of nitric oxide, when kindled burns with a brilliant blue flame.

A mixture of hydrogen and nitric oxide when passed over heated platinum 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. Beyond a certain dilution the acid absorbs very little of the gas.

The composition of nitric oxide may be determined by heating a piece of potassium in a confined volume in a bent tube over mercury, or a spiral of iron wire may be heated strongly by an electric current

in a measured volume of gas (Fig. 278). The oxygen is removed by the potassium or the iron, and after cooling the nitrogen occupies half the original volume of gas. 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.

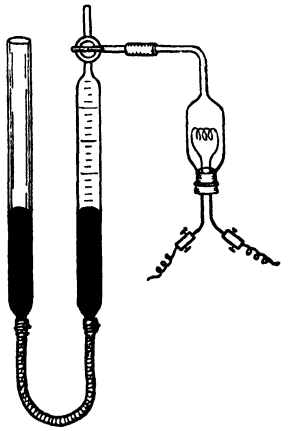


FIG. 278.—Composition of nitric oxide

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) is 30·009; or N = 30·009 – 16 = 14·009. The apparatus is shown in Fig. 279. 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 increase in weight of *A* gave the weight of oxygen which had combined with the nickel. $2NO + 2Ni = N_2 + 2NiO$.

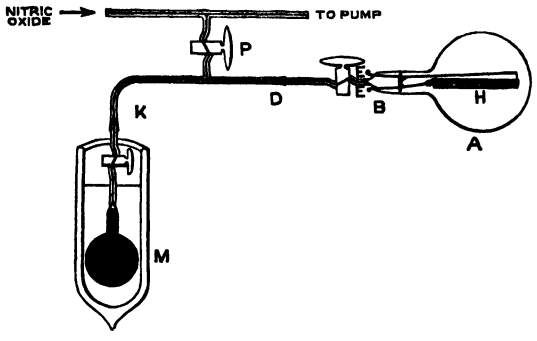


FIG. 279.—Gray's apparatus for determining the composition of nitric oxide.

Nitrous oxide.—Priestley in 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 (N_2) left by common air in supporting combustion vigorously. Priestley called the gas *dephlogisticated nitrous air*. It was carefully examined by Davy in 1799, who prepared it in the pure state by a method discovered by

Berthollet in 1785, viz. by heating ammonium nitrate. Davy determined its composition, and examined its physiological action. He called it nitrous oxide. Its use as an anaesthetic and its peculiar effects ("laughing gas") are well known.

Nitrous oxide is not easily synthesised D. L Chapman, Goodman and Shepherd (1926) obtained it by passing an electric discharge through nitrogen at low pressure in a tube of fused silica, the walls of which had previously been saturated with oxygen by passing a discharge through that gas in the tube

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:

$$2NO + SO_2 + H_2O = H_2SO_4 + N_2O$$
$$4Zn + 10HNO_3 \text{ (dilute)} = 4Zn(NO_3)_2 + 5H_2O + N_2O$$
$$2HNO_3 + 4SnCl_2 + 8HCl = 4SnCl_4 + 5H_2O + N_2O.$$

The gas is most conveniently obtained by the decomposition of ammonium nitrate by heat: $NH_4NO_3 = N_2O + 2H_2O$. This gas may contain some nitrogen Very pure nitrous oxide is obtained by mixing solutions of equimolecular amounts of hydroxylamine hydrochloride and sodium nitrite: $NH_3O + HNO_2 = N_2O + 2H_2O$.

EXPT. 9.—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 $NH_4NO_3 = N_2O + 2H_2O + 25$ k 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. It may still contain a few per cent. of nitrogen.

Nitrous oxide is prepared for use as a mild anaesthetic; it is carefully purified from chlorine and nitric oxide and liquefied by compression in steel cylinders.

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, and more soluble in alcohol. The volumes at S.T.P. absorbed are:

Temperature -	0°	5°	10°	15°	20°	25°
1 vol. of water -	1·3052	1·0954	0·9196	0·7778	0·6700	0·5962
1 vol. of alcohol -	4·178	3 844	3·541	3·268	3·025	—

The aqueous solution has no action on litmus, so that the gas does not behave as the true anhydride of hyponitrous acid: $H_2O + N_2O = H_2N_2O_2$, although it is formed by its spontaneous decomposition. When cooled to $-90°$, or exposed to pressure (30 atm. at 0°; 50 atm. at 15°), it forms a colourless mobile liquid, b. pt. $-88{\cdot}7°$; the critical temperature is 36·5°, the critical pressure 71·66 atm. The density of the liquid at the b. pt. is 1·26; when cooled in liquid air, 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. $-102{\cdot}3°$.

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 easily as air or nitrous oxide. This is probably because nitrous oxide is more easily decomposed by heat than nitric oxide, which is stable to about 1000° Decomposition of nitrous oxide begins at 520°, and is complete at 900°. At lower temperatures the principal reaction is $2N_2O = 2N_2 + O_2$, but at 1300° the reaction $2N_2O = 2NO + N_2$ also occurs The gas is decomposed by sparks; some nitric oxide is also formed. Combustion in *nitric* oxide, once begun, is more brilliant than in nitrous oxide.

Expt. 10.—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 a red gas with nitric oxide.

Expt. 11.—Brightly burning phosphorus burns in the gas with a brilliant flame, producing clouds of pentoxide, and a little red 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 A hydrogen flame is greatly enlarged in nitrous oxide. The ignition points of hydrogen, ethylene and propylene are lower in nitrous oxide than in oxygen or air, probably owing to the catalytic effect of traces of nitric oxide formed.

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 alkaline pyrogallol, 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 heated 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 (Davy, 1799). 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:

$$\underset{20\text{ c c}}{N_2O} + H_2 = \underset{20\text{ c c}}{N_2} + \underset{20\text{ c.c.}}{H_2O},$$

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 cc. 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.

Nitrous acid and nitrites.—Scheele (1774) observed that the residue left after heating nitre effervesced with acids and gave a red gas, hence he concluded that it was a salt of a new acid: it 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, since nitrites decompose at a high temperature:

$$4NaNO_2 = 2Na_2O + 2N_2 + 3O_2,$$

and this dissolves lead oxide. Lead is precipitated by carefully neutralising with nitric acid. The crystals of **sodium nitrite** are dried in a centrifuge, then in an oven at 50°. They have a yellowish colour and usually contain some nitrate. Potassium nitrite may be obtained similarly but does not crystallise well, hence it is precipitated from the solution by alcohol or is fused and cast into sticks.

Purer nitrites are formed by passing the red gas evolved on heating nitric acid with arsenious oxide, consisting of a mixture of nitric oxide and nitrogen dioxide, $NO + NO_2$, into a solution of alkali (sp gr. 1·38) or carbonate 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 .

$$C_5H_{11}NO_2 + KOH = C_5H_{11}OH \text{ (amyl alcohol)} + KNO_2$$

Both potassium and sodium nitrites are slightly yellow and their concentrated solutions are markedly yellow. The solutions are not alkaline when the salts are pure. Sodium nitrite fuses at 217°, and 4 parts dissolve in 5 parts of water at 15°. Its crystals are thin flat prisms, moderately deliquescent ; it may be purified by recrystallisation (unlike KNO_2). Potassium nitrite, m. pt. 297·5°, occurs in minute short prisms containing no water, not deliquescent when quite pure, and soluble in one-third its weight of water.

Barium nitrite is 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 yellowish-white, sparingly soluble (0·33 gm. in 100 water at 15°) precipitate, when alkali nitrite is added to silver nitrate solution. It is purified by recrystallisation from hot water.

If a dilute acid, even acetic, is added to a nitrite solution, free **nitrous acid,** HNO_2, is formed but decomposes, oxides of nitrogen being liberated. The solution has a pale blue colour, due not to nitrous acid but to **nitrous anhydride,** N_2O_3, which has a deep blue colour in the liquid state.

The decomposition of the nitrous acid in fairly concentrated solutions is probably :

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \rightleftharpoons NO + NO_2 + H_2O.$$

In dilute solutions it decomposes according to the equation :

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

The amount of nitrous acid or 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. The free acid can be titrated with caustic soda and alizarin red as indicator.

Nitrous acid and nitrites are *reducing* agents: $HNO_2 + O = HNO_3$; they reduce permanganates and chromates. They may be estimated in solution by running into excess of warm acidified $N/2$ potassium permanganate, and titrating the excess 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 sometimes act as *oxidising* agents: $2HNO_2 = 2NO + O + H_2O$. Iodine is liberated from potassium iodide:

$$2KI + 2HNO_2 = 2KOH + I_2 + 2NO,$$

indigo is bleached, stannous chloride is oxidised to stannic chloride:

$$SnCl_2 + 2HCl + 2HNO_2 = SnCl_4 + 2NO + 2H_2O,$$

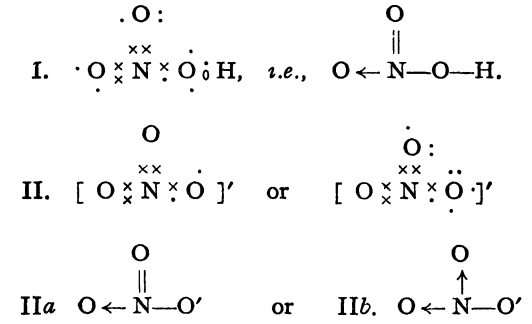
sulphur is precipitated from hydrogen sulphide, and sulphur dioxide is oxidised to sulphuric acid In presence of atmospheric oxygen, NO will reproduce nitrous acid, so that a small amount of nitrous acid may effect a considerable amount of oxidation by acting as a carrier of oxygen, *i.e.*, as a catalyst

The liberation of iodine from potassium iodide (blue colour with starch) is a test for nitrous acid or a nitrite in acid solution. Still more delicate tests are (i) the brown colour with a solution of meta-phenylenediamine hydrochloride in hydrochloric acid, and (ii) 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 estimation of nitrites in water.

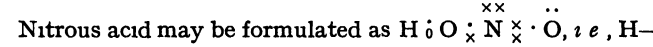
Nitrites detonate violently when heated with thiosulphates or cyanides, so that care must be used in heating solid mixtures of nitrates with reducing substances which can form these bodies A mixture of sulphur, potassium carbonate and nitre, or of nitre and potassium cyanide, detonates violently when heated These mixtures are sometimes encountered in qualitative analysis.

The constitution of oxygen compounds of nitrogen.—The constitutional and electronic formulae of the oxides and oxy-acids of nitrogen offer peculiar difficulties and are at present uncertain in some cases. The

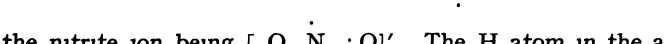
formulae of nitric and nitrous acids and their ions, of nitric anhydride and of the nitro-group in organic nitro-compounds are regarded as very probable, and it is known that the molecule of nitrous oxide is linear and not symmetrical (*i e*, the oxygen atom is at the end), but the formulae of the remaining compounds are mostly speculative. The electronic formulae of nitric acid (I) and of the nitrate ion (II) may be written :



It is possible that the structure of the acid (I) is preserved in the organic nitric esters, such as ethyl nitrate, $C_2H_5NO_3$, but that in metal salts the second form of the ion, II*b*, is present. The nitrate ion in solid salts is shown by X-rays to be a flat equilateral triangle with the nitrogen in the centre and the three oxygens at the vertices (cf the carbonate ion, pp 433, 506)



Nitrous acid may be formulated as H—O—N=O, *i e*, H—O—N=O,



the nitrite ion being [. O N . · O]′ The H atom in the acid, or the radical R in the esters (*e g*., $C_2H_5NO_2$, ethyl nitrite), is directly attached to oxygen · the esters on reduction yield alcohol and ammonia (with some hydroxylamine, p. 555) : $RO\,N=O+6H=ROH+NH_3+H_2O$. In the nitro-compounds, *e.g.*, $C_2H_5NO_2$, nitroethane, isomeric with nitrites, and formed by the action of silver nitrite on alkyl iodides, the radical is directly attached to nitrogen, since on reduction they yield amines $R\,NO_2+6H=R{\cdot}NH_2+2H_2O$. In the nitro-group, $-NO_2$, one oxygen is attached by a double bond and the other by a semipolar double bond (p. 352) :

R—N=O, *i.e*, R—N=O.

Nitrogen never exhibits a covalency greater than four, the old formulae involving quinquevalent nitrogen being incorrect (cf. p. 779). Silver and mercurous nitrites are pale yellow solids and may have the nitro-group structure.

The structures of the oxides of nitrogen may be as follows.

N_2O $\dot{\dot{N}} :: N :: O$, a linear molecule (p 225).

NO $\overset{\times\times}{\underset{\times\times}{N}} :: \dot{\dot{O}}\cdot$ containing an odd electron and about half as magnetic as the oxygen molecule, with two odd electrons

$$O :: \dot{O}\cdot$$

N_2O_3 $\dot{\dot{O}} :: N :: O :: N :: \dot{O}$

NO_2 $O :: N :: O$ or $:O :: N :: \dot{\dot{O}}$, containing an odd electron but only feebly magnetic, the double molecule N_2O_4, also N_2O_3, N_2O and N_2O_5 are diamagnetic.

N_2O_4 $\dot{\dot{O}}\ N\ O$ / $\dot{O}..N..O$

N_2O_5 $:O\cdot \quad O$ / $:O :: N :: O\cdot O :: N :: O:$

Nitrous anhydride or nitrogen trioxide.—Red vapours obtained by distilling diluted nitric acid with arsenious oxide or starch, on cooling in a freezing mixture, give a dark blue volatile liquid: $2HNO_3 + As_2O_3 = As_2O_5 + H_2O + N_2O_3$.

EXPT 12.—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 and connected by a paraffined cork with a glass worm cooled with ice and salt (Fig. 251). 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 by caustic-soda solution with formation of sodium nitrite, and by concentrated sulphuric acid with formation of nitrososulphuric acid. It therefore behaves as if it were nitrous anhydride, N_2O_3:

$$2NaOH + N_2O_3 = 2NaNO_2 + H_2O.$$

$$2SO_2(OH)_2 + NO\cdot O\cdot NO = 2SO_2(OH)\cdot O\cdot NO + H_2O.$$

The vapour density shows, however, that it is a mixture of equal volumes of nitric oxide and nitrogen dioxide, so that N_2O_3 is almost completely dissociated into NO and NO_2.

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

$NO + NO_2 = N_2O_3$ (contraction $\frac{1}{2}$) ; $2NO + N_2O_4 = 2N_2O_3$ (contraction $\frac{1}{3}$)

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 : $N_2O_3 \rightleftharpoons NO + NO_2$. (H. B and M Baker, 1907.)

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 $-102°$, and (unless quite dry) begins to decompose at $-21°$.

A mixture of nitric oxide with oxygen or air, if rapidly made in presence of alkali, is quickly absorbed with formation of nitrite only, and thus behaves as if it contained N_2O_3:

$$3NO + O_2 = NO + NO_2 \rightleftharpoons N_2O_3;$$
$$N_2O_3 + 2KOH = 2KNO_2 + H_2O.$$

The mixture of gases, if first allowed to stand, is more slowly absorbed by alkali, with formation of both nitrite and nitrate ; the nitric oxide is completely oxidised to nitrogen dioxide

$$2NO_2 + 2KOH = KNO_2 + KNO_3 + H_2O.$$

EXPT 13.—To 20 c c. of pure NO in a 3 cm diameter tube over mercury containing 10 c c. of conc KOH add rapidly 25 c c. of air. Almost immediate absorption of the red gas occurs and 20 c c. of N_2 remain To 10 c.c. of NO in a second tube, without alkali, add 25 c c. of air and after 2 minutes add 10 c.c. of potash. The red gas is absorbed and 20 c c of N_2 remain (Gay-Lussac, 1816).

By means of a T-tube admit a *small* amount of NO into a *rapid* stream of air passing into a large flask 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

These reactions have 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, but they may be explained by the slowing down of the speed of oxidation of NO to NO_2 when half the oxidation in the termolecular reaction has been effected.

Nitrogen dioxide and tetroxide.—If nitric oxide is mixed with oxygen or a gas containing free oxygen, a red gas is produced. This consists of nitrogen dioxide: $2NO + O_2 = 2NO_2$. At temperatures below 140° a portion 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 dry, is passed *slowly* through a large bulb so as to allow time for complete oxidation, and the gas then passed through a spiral tube cooled in a freezing mixture, yellow liquid nitrogen tetroxide is condensed. But the reaction $2NO + O_2 = 2NO_2$ requires time for completion, and if the mixed gas is passed *rapidly* into a cooled tube a green liquid condenses, which 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:

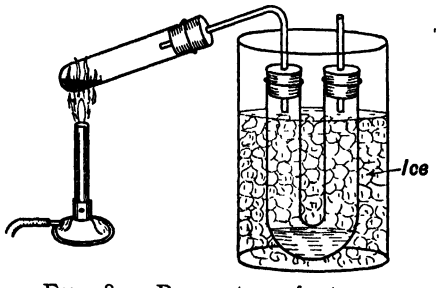


FIG 280.—Preparation of nitrogen dioxide from lead nitrate

$$4NO_2 + H_2O = 2HNO_3 + N_2O_3.$$

The velocity of the reaction $2NO + O_2 = 2NO_2$ *decreases* with rise in temperature; at $-184°$ it is 100 times as fast as at 0°.

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 nitrate by heat.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

EXPT. 14.— Heat *dry* powdered lead nitrate in a hard glass tube, and pass the gas evolved through a U-tube cooled in a mixture of ice and salt (Fig 280). A yellow liquid collects 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 rich in N_2O_3 separates $2N_2O_4 + 2H_2O \rightleftharpoons 2HNO_2 + 2HNO_3 \rightleftharpoons N_2O_3 + 2HNO_3 + H_2O$ (Fritzsche, 1840).

This is not a very satisfactory method of preparing nitrogen dioxide in quantity. More convenient is 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. 15.—To the blue liquid obtained in EXPT 12, 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 ("chamber crystals") with dry potassium nitrate:

$$SO_2(OH)\cdot O\cdot NO + KNO_3 = N_2O_4 + KHSO_4.$$

EXPT 16.—Pass sulphur dioxide *slowly* into well cooled fuming nitric acid in a retort until the liquid becomes a pasty mass of crystals of nitrososulphuric acid Add dry potassium nitrate, stopper the retort, heat gently 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 $-9{\cdot}04°$ 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 some NO_2, which is strongly coloured. On warming, the colour deepens; at 10° it is yellow, at 15° orange, and darkens until at $21{\cdot}9°$ it is reddish-brown, and then the liquid boils, giving a red vapour. The colour of the vapour darkens on further heating, as may be seen by comparing two globes containing it, one maintained at the ordinary temperature: at 40° it has a very deep, almost black, colour.

The colour change on heating at atmospheric pressure is accompanied by a decrease in vapour density up to 140°, when it becomes constant and corresponds with NO_2: the intermediate densities correspond with the dissociation: $N_2O_4 \rightleftharpoons 2NO_2$.

Temperature.	Vapour density	Percentage dissociation.
26·7°	38·3	20·1
60·2	30·1	52·8
100·1	24·3	89·3
135·0	23·1	99·1
140·0	22·96	100·0

On heating the vapour above 140°, the vapour density further decreases but the colour becomes paler, until at 620° the gas is colourless owing to 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:

$$N_2O_4 \text{ solid} \underset{-9{\cdot}04^\circ}{\rightleftharpoons} N_2O_4 \text{ liq.} \underset{21{\cdot}9^\circ}{\rightleftharpoons} N_2O_4 \text{ (vap.)} \underset{140^\circ}{\rightleftharpoons} 2NO_2 \underset{620^\circ}{\rightleftharpoons} 2NO + O_2.$$

The composition of nitrogen dioxide is ascertained by passing it over copper heated to *bright* redness (otherwise NO is formed):

$$4Cu + 2NO_2 = 4CuO + N_2$$

Nitrogen dioxide vapour does not readily support the combustion of a taper, but strongly burning phosphorus and carbon burn in it. The gas is probably decomposed into nitrogen and oxygen, or nitric oxide and oxygen. Potassium inflames spontaneously in the gas, heated sodium burns in it; and a spiral of heated iron wire 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 heated platinum: $2NO_2 + 7H_2 = 2NH_3 + 4H_2O$.

Nitrogen dioxide is absorbed by concentrated sulphuric acid with formation of nitrososulphuric acid and nitric acid, and 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. Quicklime, and oxides of zinc, aluminium, and lead, absorb the gas on heating, but free nitrogen and nitric oxide are liberated

in the case of quicklime (Oswald, 1914). These gases are formed from the calcium nitrite first produced (Partington and Williams, 1924) :

$$2CaO + 4NO_2 = Ca(NO_3)_2 + Ca(NO_2)_2;$$
$$Ca(NO_2)_2 + 2NO_2 = Ca(NO_3)_2 + 2NO,$$
$$Ca(NO_2)_2 + 2NO = Ca(NO_3)_2 + N_2$$

Nitrogen dioxide reacts with copper forming cuprous oxide, which then absorbs a further quantity of the gas $2Cu + NO_2 = Cu_2O + NO$ (Park and Partington, 1924) . the so-called " nitro-copper " produced is not a definite substance

Pernitric acid.—Hautefeuille and Chappuis, and Berthelot (1881), claimed to have obtained a higher oxide, N_2O_6, by the action of a silent discharge on a mixture of nitrogen peroxide and oxygen with water it was supposed to form pernitric acid, HNO_4 Bromine is liberated from KBr solution by a mixture of H_2O_2 and nitric acid, but not by either separately Pernitric acid is said to be formed by the action of pure H_2O_2 on N_2O_5.

Hyponitrous acid.—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 has the empirical formula AgNO, and is a salt of hyponitrous acid Subsequent investigations showed that the acid really has the doubled formula $H_2N_2O_2$.

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 over 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

Hyponitrous acid is also formed in small quantities by the action of nitrous acid on hydroxylamine :

$$HO - N H_2 + O : N{\cdot}OH = HO{\cdot}N : N{\cdot}OH + H_2O.$$

Expt. 17.—To a solution of hydroxylamine sulphate add sodium nitrite solution. Heat rapidly to 60°, then add silver nitrate solution. A *canary yellow* precipitate of silver hyponitrite is formed. If the conditions are not correct, a yellowish-white precipitate of silver nitrite is obtained.

Sodium hyponitrite is produced by warming sodium hydroxylamine sulphonate with caustic soda : $2HO{\cdot}NH{\cdot}SO_3Na + 4NaOH = Na_2N_2O_2 +$

$2Na_2SO_4 + 4H_2O$ It is prepared by passing nitric oxide through sodium dissolved in liquid ammonia, or the sodium compound of pyridine suspended in benzene $2Na + 2NO = Na_2N_2O_2$, and is formed by the reduction of potassium nitrososulphate with sodium amalgam

$$N_2O_2SO_3K_2 + 2Na = Na_2N_2O_2 + K_2SO_3$$

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 laminae of free hyponitrous acid, $H_2N_2O_2$, are formed The solution decomposes with evolution of nitrous oxide : $H_2N_2O_2 = H_2O + N_2O$.

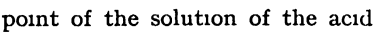
Hyponitrites in acid solution reduce permanganate : $5H_2N_2O_2 + 8KMnO_4 + 12H_2SO_4 = 10HNO_3 + 4K_2SO_4 + 8MnSO_4 + 12H_2O$. In alkaline solution a nitrite is formed

The 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 $H_2N_2O_2$

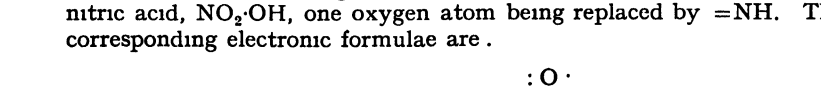
3 By the action of ethyl iodide on silver hyponitrite, ethyl hyponitrite is obtained, the molecular weight of which corresponds with the formula $(C_2H_5)_2N_2O_2$

4 The esters have no dipole moment, hence the formula of hyponitrous acid is HO—N / N—OH. The electronic formula is 

Nitramide.—By the nitration of potassium imidosulphonate under special conditions, and hydrolysis, an isomer of hyponitrous acid called nitramide is formed

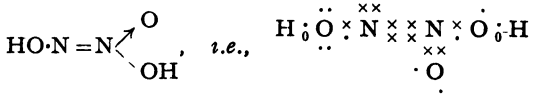
$$HN(SO_3H)_2 \rightarrow NO_2{\cdot}N\underset{2H}{(SO_3H)_2} \rightarrow NO_2{\cdot}\underset{OH}{NH_2} + 2H_2SO_4$$

Thiele and Lachmann represented it as HN NO(OH), *i e*, the imide of nitric acid, $NO_2{\cdot}OH$, one oxygen atom being replaced by =NH. The corresponding electronic formulae are.



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 decom-

posed 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



Nitrosyl chloride.—A mixture of 1 vol of concentrated nitric acid and 4 vols. of concentrated hydrochloric acid, called by the alchemists *aqua regia* because it is capable of dissolving gold (" the king of metals "), owes this action to the presence of free chlorine On warming *aqua regia*, an orange-yellow mixture of chlorine and nitrosyl chloride is evolved (Gay-Lussac, 1848) $HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$ The gas is dried by calcium chloride and passed through concentrated sulphuric acid · chlorine passes on, whilst the nitrosyl chloride is absorbed as nitrososulphuric acid: $NOCl + SO_2(OH)_2 = SO_2(OH)\cdot O\cdot NO + HCl$. When the acid is warmed with sodium chloride, pure nitrosyl chloride is evolved.

$$SO_2(OH)\cdot O\cdot NO + NaCl = SO_2(OH)ONa + NOCl.$$

Nitrosyl chloride is formed by the direct combination of nitric oxide and chlorine in bright sunlight, or in presence of animal charcoal at 40°–50°: $2NO + Cl_2 = 2NOCl$, and since it is the acid chloride of nitrous acid, 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. −5·5°, freezing to a lemon-yellow solid, m. pt. −64 5°. 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; whilst with $MnCl_2$ and $FeCl_2$, the compounds $MnCl_3\cdot NO$ and $FeCl_3\cdot NO$ are formed.

Nitrosyl bromide, NOBr, a blackish-brown liquid, b. pt. −2°, is formed by passing nitric oxide into bromine at −15°. At the ordinary temperature $NOBr_3$ is formed **Nitrosyl fluoride,** NOF, a gas, b. pt. −59·9°, m pt. −132 5°, is 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, **nitryl chloride**, NO_2Cl, is obtained as a colourless gas, liquid at $-15°$, by the action of ozone on nitrosyl chloride $NOCl + O_3 = NO_2Cl + O_2$ The fluoride, **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. $-72\ 4°$, m pt. $-166°$.

Nitrososulphuric acid, or "chamber crystals."—This compound, supposed to be formed as an intermediate stage in the lead chamber process, can be obtained in a number of ways. It was obtained by Clement and Desormes in 1806 by the interaction of oxides of nitrogen, sulphur dioxide, and a regulated amount of moisture :

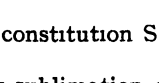
$$3NO_2 + 2SO_2 + H_2O = 2SO_2(OH)\cdot O\cdot NO + NO$$

It is more conveniently prepared by passing the red vapours from arsenic trioxide and nitric acid into cooled concentrated sulphuric acid : $NO + NO_2 \rightleftharpoons N_2O_3 + 2H_2SO_4 \rightleftharpoons 2SO_2(OH)\cdot O\cdot NO + H_2O$. The substance decomposes with effervescence, evolving red fumes, when treated with water, so that the reaction is reversible It dissolves in concentrated sulphuric acid and in sulphuric acid containing not more than 35 per cent of water, but in more dilute acid decomposition occurs, and the nitrogen compounds are then almost completely expelled on heating.

Nitrososulphuric acid is best prepared by passing sulphur dioxide into cooled fuming nitric acid and draining the white crystals on a porous tile in a desiccator

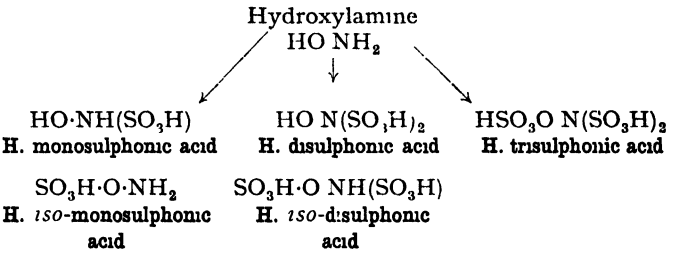
$$SO_2 + HNO_3 = SO_2(OH)\cdot O\cdot NO.$$

Nitrososulphuric acid, $NO\cdot O\cdot SO_2(OH)$ is sometimes called **nitrosulphonic acid**, $NO_2\cdot SO_2\cdot OH$. It may also be formulated as **nitrosyl sulphate**, $NO\cdot HSO_4$. The crystals melt with decomposition at $73°$; water is split off and a white crystalline substance, m. pt. $217°$, b pt. $360°$, **dinitropyrosulphuric acid**, $S_2O_5(O\cdot NO)_2$, is formed

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 in benzene, or on thionyl chloride. It melts at $178°$, 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 **thiotrithiazyl chloride**, N_3S_4Cl, which is converted by nitric acid into a crystalline nitrate, $N_3S_4\ NO_3$ The molecular weight of nitrogen sulphide in solution corresponds with the formula N_4S_4; it is supposed to have the constitution  . A blue modification of N_4S_4 is obtained by sublimation of the ordinary form over silver gauze. Nitrogen pentasulphide, N_2S_5, is formed as a deep

red liquid, m pt 10°–11°, when N_4S_4 is treated with carbon disulphide at 100° It decomposes on heating.

Sulphonic acids of ammonia and hydroxylamine.—The following isomeric compounds are all sulphonic acid derivatives of hydroxylamine, *i.e.*, H is substituted by $-SO_2OH$



Some products of the action of nitrites on sulphites have already been described (p. 556)

The first product appears to be **hydroxylamine disulphonic acid :**

$$HO{\cdot}NO + 2H\,SO_3H = HO\,N(SO_3H)_2 + H_2O$$

This may undergo hydrolysis or further sulphonation .

$$HO{\cdot}N(SO_3H)_2 + H_2O = HO\,NH\,SO_3H \text{ (hydroxylamine monosulphonic acid)} + H_2SO_4$$

$$HO\,N(SO_3H)_2 + H\,SO_3H = N(SO_3H)_3 \text{ (nitrilosulphonic acid)} + H_2O$$

These substances are intermediate products in the oxidation of sulphurous to sulphuric acid by means of nitrous acid

By the action of KNO_2 on $KHSO_3$ in solution the following reaction occurs

$$KNO_2 + 3KHSO_3 = HO\,N(SO_3K)_2 + K_2SO_3 + H_2O$$

On adding lead dioxide the potassium salt of **hydroxylamine trisulphonic acid** is formed (Fremy, 1845 , Haga, 1904) .

$$HO\,N(SO_3K)_2 + K_2SO_3 + PbO_2 = (KSO_3)O\,N(SO_3K)_2 + PbO + KOH$$

With very dilute acid this splits off one SO_3K attached to nitrogen, giving a salt of **hydroxylamine** *iso*-**disulphonic acid,** $KSO_3\,O{\cdot}NH{\cdot}SO_3K$ (Raschig, Haga, 1906) **Hydroxylamine** *iso*-**monosulphonic acid** is obtained by the action of chlorosulphonic acid on hydroxylamine salts (Sommer, 1914) .

$$NH_2OH + ClHSO_3 = HCl + NH_2{\cdot}O\,SO_3H.$$

It is the amide of Caro's acid, has oxidising properties and liberates iodine from KI.

By oxidising $HO{\cdot}N(SO_3H)_2$ with lead peroxide, a deep blue solution of **peroxyl-amino-disulphonic acid,** probably $(SO_3H)_2{=}N{=}O$ is formed. The potassium salt is blue in solution, but forms yellow crystals.

The action of sulphur dioxide on nitrososulphuric acid (" chamber crystals ") produces an unstable purple **nitrosisulphonic acid,** HO–N(O)–SO_3H, which readily decomposes with evolution of nitric oxide. $H_2SNO_5 = H_2SO_4 + NO$ This is also formed by the oxidation of hydroxylamine monosulphonic acid with persulphuric acid A purple ferrous salt is readily formed when nitric oxide is passed into a suspension of ferrous sulphate in concentrated sulphuric acid, and seems to be the cause of the purple colour formed in the " brown ring test " when only small amounts of nitrates are present

Nitrilosulphonic 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,** $NH(SO_3H)_2$ $N(SO_3K)_3 + H_2O = NH(SO_3K)_2 + KHSO_4$ On further hydrolysis, salts of **amidosulphonic acid,** NH_2SO_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.

CHAPTER XXXI

THE INACTIVE ELEMENTS

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 it with oxygen over caustic potash. 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, 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 = 1·2505; (*b*) atmospheric nitrogen = 1·2572 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 (Ramsay); (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 281. 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 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. 282) 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

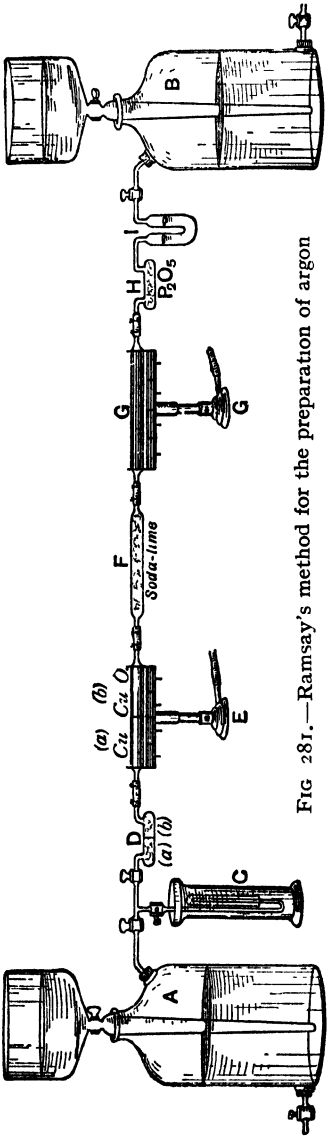


FIG 281.—Ramsay's method for the preparation of argon

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, in 1895, stated that a contraction occurred when a mixture of argon and benzene vapour was subjected to the silent discharge, but this is unconfirmed.

The separation of atmospheric argon is carried out on the technical scale, since the gas is in demand for filling metal-filament electric lamps If these are vacuous, the tungsten filament volatilises and a black film is deposited on the inside of the bulb 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 at 800° in iron retorts. The nitrogen and oxygen are absorbed, the former as calcium cyanamide, the latter as calcium carbonate, and the residual gas after passing over heated copper oxide to oxidise carbon monoxide to dioxide (which is absorbed by potash), is dried About 3 per cent of argon is present in the liquid oxygen from air. The oxygen is removed from the gas obtained by evaporation, by passing over heated copper or by a hydrogen flame, and the residual gas is 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 is used for filling electric lamps. Argon obtained by all processes contains other inactive gases (*e g*, krypton) in traces.

In the residue from the evaporation of liquid air Ramsay and Travers (1898) discovered two other 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 (at wt 20) was searched for in order to fill a gap in the periodic system between helium (at wt. 4) and argon (at wt 40). The examination of the residues from the evaporation of 120 tons of liquid air failed to indicate the presence of any other gases. The inactive elements 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 partly due to removal of traces of other gases by the discharge. In the absence of these, the inactive gases become fluorescent or even non-conducting.

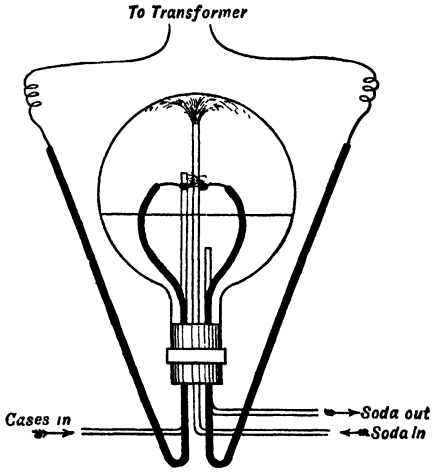


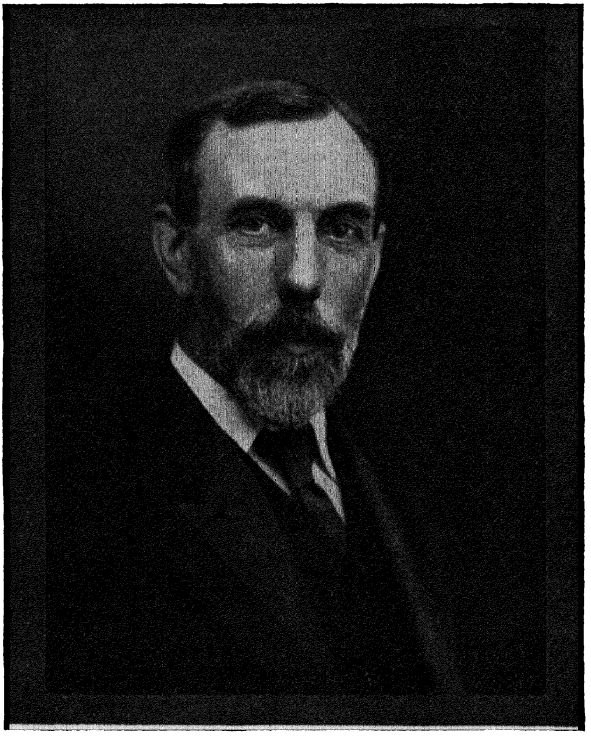
FIG 282.—Rayleigh's method for the preparation of argon.

Inactive gases are 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. Some springs yield a gas containing 10 per cent. of helium, usually the amount is much smaller. The water of these springs is slightly radioactive, but according to Moreu this has nothing to do with the inert gases Rayleigh and Ramsay found that the gas evolved on heating rain water contains twice as much argon as air

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 Sir Norman Lockyer concluded that it corresponded with an element not present in terrestrial substances, to which he 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.

Doubts having been cast on the homogeneity of the gas, Ramsay and Travers (1897) showed by an exhaustive fractional diffusion that



SIR WILLIAM RAMSAY.

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 natural gas from Medicine Hat, Canada; and Texas, Utah and Colorado, U.S.A., some specimens of which contain 8 per cent. by volume of helium, although less than 1 per cent. is usual. It is prepared from natural gas by strong cooling, when all other gases condense.

The industrial sources of helium have in recent years attracted a considerable amount of attention in view of the use of this gas in place of hydrogen for filling the gas containers of airships In the United States a considerable amount of helium extracted from natural gas is available and in use. An alternative source of helium which is of great interest in the possible applications of the gas in the British Empire is the mineral *monazite*, the raw material for the production of thoria for incandescent gas mantles, which is found in large quantities at Travancore, India. The mineral contains about 1 c.c. of helium per gram, and thus in the working up of every 100 tons of monazite about 100,000 litres of helium are allowed to escape into the atmosphere. The gas escapes on heating

Helium occurs in small quantities in numerous minerals and may be the result of **radioactive changes.** The gas, although present only in minute quantities in the atmosphere (1 vol in 200,000), may be separated by a slight modification of the Claude rectifier for the treatment of liquid air.

Helium is readily purified from other gases by making use of the discovery of Dewar (1904) that coconut 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 Helium can diffuse through glass at the ordinary temperature (Paneth, 1928).

Liquid helium was 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 −268·82° ; by the rapid evaporation of the liquid at very low pressures, the temperature was reduced to 0·82° above the absolute zero, but the helium was still liquid. At this temperature the electrical resistance of some 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. **Solid helium** was obtained by Keesom in 1926 by cooling the liquid to about −272° (1° abs.) *under pressure*

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 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 some types of electric lamps

The group of inactive gases contains also the **emanations** of radium, thorium and actinium These are isotopes, but have different radio-active constants and are called **radon** (discovered by Dorn, 1901), **thoron** (Rutherford and Soddy, 1900) and **actinon** (Giesel, 1902, Debierne, 1903) (Chapter XXV).

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 radon 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	Radon
Atomic Number -	2	10	18	36	54	86
Electron configuration -	2	2 8	2 8 8	2·8 18 8	2 8 18· 18 8	2·8 18· 32·18 8
Normal density	0·17846	0·89990	1·78364	3 708	5 851	9 97
Atomic weight	4 000	20 182	39 943	82 92	130 2	222 4
Critical temperature	−267·90°	−228·70°	−122·44°	−62·5°	+16·6°	104 5°
Critical pressure (atm)	2·26	26 86	47 996	54 3	58 2	62·4
Boiling point -	−268·87°	−245·92°	185 85°	−151 8°	−109 2°	−65°
Melting point	−272°	−248·52°	189·25°	−169°	−140°	−71°
Compressibility λ (p 121)	−0·0005	−0·0004	+0 001	+0 0025	+0 0069	+0 018
Absorption coeff. in water at 0° - -	0·00967	0·0114	0 0053	0·1105	0 242	0·51

Helium is the least soluble of all gases. The inert gases form crystalline hydrates by compressing with water and releasing the pressure. The most stable is that of xenon, with 6 or $7H_2O$, the dissociation pressure of which is 1·15 atm. at 0°.

The monatomic character of the gases is indicated by the value of the ratio of the specific heats, $\gamma = 1{\cdot}667$, 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 this is called the **zero-group**, Group O or Group VIII *b* when they are regarded as closing a period. They bridge the gap between the strongly electropositive elements of the first group and the strongly electronegative elements of the seventh group.

CHAPTER XXXII

PHOSPHORUS

The nitrogen group.—Group V. in the Periodic System comprises, besides radio-elements, 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 properties of the elements of the odd series are as follows .

	N	P.	As	Sb	Bi.
Atomic number	7	15	33	51	83
Electron configuration	2·5	2·8·5	2·8·18·5	2·8·18·18·5	2·8·18·32·18·5
Sp. gr. of solid	1·0265	1·83 (yellow) / 2 20 (red)	5·73	6·67	9 80
Atomic volume	13·65	16·96 (yellow)	13·08	18·25	21·32
Melting point	−210°	44·1°	814·5°	630 5°	271°
Boiling point	−195·8°	280·5°	615° sublimes	1380°	1450°

In the typical compounds of the elements the latter are usually ter- or quinque-valent, but occasionally quadrivalent. The hydrides 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 are derived from Sb_2O_3 and Bi_2O_3, *e.g.*, $Bi(NO_3)_3$. 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 1669–74, a physician of Hamburg, Brand, obtained a remarkable substance by distilling evaporated urine with sand and carbon. It had the property of shining, the glow being visible in the dark, and was called phosphorus (Greek *phos*, light, *phero*, I bear). Decomposed 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 at the Court of Charles II in 1677. Here it was seen by Boyle. The latter in 1680, and Kunckel in Berlin in the year 1678, independently rediscovered the method of preparation. 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. 829), which emits similar light, but only after previous exposure to sunlight. Gahn, about 1770, discovered calcium phosphate, $Ca_3(PO_4)_2$, in bones, and Scheele 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, they 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, *Redonda phosphate* (35–40 per cent P_2O_5), a cheap and rich ore from the West Indies, is aluminium phosphate, $AlPO_4$, *vivianite* is ferrous phosphate, $Fe_3(PO_4)_2,8H_2O$. The softer ores are used in the manufacture 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 *glycero-phosphates*.

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 salts. In order to repair the tissue-waste and to provide phosphates for the structure of bones, phosphorus compounds 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 are therefore valuable fertilisers.

Phosphorus occurs in an inorganic form in *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, and the degreased bones heated strongly out of contact with air in iron retorts, the organic matter is decomposed and animal charcoal remains, used in decolorising sugar syrup. When no longer active, it is calcined in the air, the carbonaceous matter burns off and bone-ash is left, consisting of about 80 per cent. of calcium phosphate, with calcium carbonate and a little fluoride.

Preparation of phosphorus.—Phosphorus was formerly prepared from bone-ash or soft mineral phosphates, decomposed by hot sulphuric acid (sp. gr. 1·5–1·6) so as to form insoluble calcium sulphate and phosphoric acid. The phosphoric acid was filtered, evaporated to a syrup, mixed with powdered coke, and distilled in fireclay retorts at a bright-red heat:

$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$ (orthophosphoric acid).
$H_3PO_4 = H_2O + HPO_3$ (metaphosphoric acid: formed on heating).
$4HPO_3 + 12C = 2H_2 + 12CO + P_4$.

Phosphorus is now made by a method proposed by Wohler (1829), viz. the direct reduction of a phosphate by carbon in presence of silica, which liberates phosphorus pentoxide at a high temperature. The technical success of the method depends on the application of the high temperature attained 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. 283).

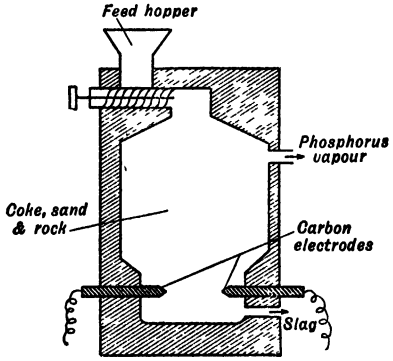


FIG 283.—Industrial preparation of phosphorus by heating a mixture of a mineral phosphate, sand and coke, in the electric furnace.

The phosphate is decomposed at a high temperature by silica, which is a very difficultly volatile weak acid anhydride.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5 \text{ (at 1150°)}.$$

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: $P_2O_5 + 5C = 2P + 5CO$. About 5 kilowatt-hours are used per kgm. 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 impurities oxidise and pass into solution and others separate 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

Most of the phosphorus output is used in the manufacture of matches. Some is used in making phosphor-bronze, as a poison for rats, and in the preparation of phosphorus trichloride, pentachloride, and pentoxide

EXPT 1.—MIX 1 gm of powdered sodium metaphosphate (obtained by heating microcosmic salt in a 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.

$$6NaPO_3 + 3SiO_2 + 10Al = 3Na_2SiO_3 + 5Al_2O_3 + 6P$$

White phosphorus.—Ordinary white phosphorus is a translucent white solid, like wax On exposure to light it becomes yellow. 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° it becomes brittle and the crystalline structure may be seen by etching the cooled stick of phosphorus in dilute nitric acid.

The specific gravity of white phosphorus is 1·83, and its melting point 44·1°. The liquid exhibits supercooling. Phosphorus boils at 287° (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 1040° 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 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 crystals. Large transparent regular crystals, usually rhombdodecahedra which exhibit a play of colours resembling that of diamond, are 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*)

A characteristic property of white phosphorus is the ease with which it undergoes oxidation when exposed to air at the ordinary temperature, the spontaneous oxidation being accompanied by a green glow, or **phosphorescence.** If gently warmed to about 50°, it catches fire in dry air and burns with a white flame, 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 2.—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 3.—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 in presence of air become covered with a white crust, which is ordinary phosphorus detached by unequal oxidation; according to Baudrimont it is not formed in water free from air. This crust slowly turns red, 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 ceased.

Red phosphorus.—This modification, formerly called "amorphous phosphorus," was prepared by Schrotter 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 k. cal. Red phosphorus is also left as a residue when white phosphorus burns in air, or in oxygen under water, and was until Schrotter's discovery considered to be a sub-oxide.

EXPT. 4.—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. 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.

Red phosphorus is made 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°, 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 It is repeatedly washed with hot water and dried with steam It usually contains about 0·5 per cent of white phosphorus, and some phosphoric acid

Red phosphorus is violet-red in colour and has a density of 2·106. 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 air until heated to about 240°. The melting point of red phosphorus, under pressure, is between 500° and 600°; when strongly heated it is converted into vapour, which on cooling deposits white phosphorus.

EXPT. 5.—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. 6.—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. Colourless drops of white phosphorus distil on to the cooler portion of the tube

White phosphorus is an unstable form: it passes slowly into red phosphorus even at the ordinary temperature when exposed to light. The vapour pressure of liquid white phosphorus at 200°, 120·4 cm., is greater than that of solid red phosphorus at 350°, 7·6 cm., and if white phosphorus is placed on one limb of a ∩-tube at 324°, and red phosphorus at 350° in the other, distillation occurs from the cooler to the hotter position.

Ordinary red phosphorus was considered to be amorphous, but Pedler and Retgers in 1890 showed that it contains 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 (*v* below) 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.

Scarlet phosphorus, obtained by Schenck by boiling a 10 per cent. solution of white phosphorus in phosphorus tribromide for ten hours, deposits as a fine scarlet amorphous powder, sp. gr 1·876, more active than common red phosphorus, but differing from white phosphorus in oxidising only very slowly in the air, and is not poisonous. 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°. $2PBr_3 + 3Hg = 3HgBr_2 + 2P$. According to Marckwald and Helmholtz (1922), phosphorus vapour when quickly cooled deposits a mixture of white phosphorus and scarlet phosphorus (which they regard as P_2); when slowly cooled it deposits white phosphorus. $2P_2 \rightleftharpoons P_4$.

Allotropic forms of phosphorus.— Besides ordinary, or **α-white phosphorus**, a second form has been described, **β-white phosphorus** formed by cooling the α-form to −76·9°, or by subjecting it to about 12,000 atm. pressure, it crystallises in the hexagonal system

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 3r6 or 2·34, which do not oxidise in air, sublime These crystals are also formed by dissolving white 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°, formed irreversibly from white phosphorus at 200° under a pressure of 12,000 kgm per sq. cm., does not ignite at 400° in air, and is a fairly good conductor of

electricity. **Violet phosphorus,** formed by heating white phosphorus with a trace of sodium to 200° under very high pressure, is crystalline, sp. gr 2·35, m. pt. 589·5°.

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 in cases of poisoning.

EXPT 7.—A small piece of phosphorus is added to water in a flask connected with a Liebig's condenser. 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 8.—The glow of phosphorus is shown in the "cold flame" experiment, due to Smithells. A few pieces of phosphorus are placed in a dry receiver, which is then filled up with glass wool. The receiver is heated on a water-bath, a stream of dry carbon dioxide being passed through (Fig 284). 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 a finger may be held in it, and it will not kindle the head of a match.

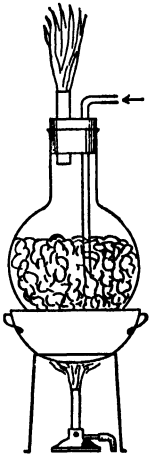


FIG. 284.—Smithells' "cold flame."

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 long 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. Fourcroy in 1788 found that phosphorus does not glow in ordinary moist oxygen at atmospheric pressure. Angelo Bellani de Monza in 1813 observed that the glow appears if the pressure of the oxygen is reduced, an observation made independently by Schweigger in 1824 and confirmed by Henry and Graham. According to Russell (1903), phosphorus glows very feebly at amospheric pressure in oxygen dried by sulphuric acid, or even at higher pressures if the surface is very clean, lower oxides of phosphorus being produced. At pressures lower than 500 mm at room temperature the glow in dry oxygen becomes much brighter and phosphorus pentoxide is formed. According to Dixon and Baker (1889) phosphorus does not glow at any pressure in oxygen dried by phosphorus pentoxide. The glow appears in ordinary oxygen if this is mixed with an inert gas.

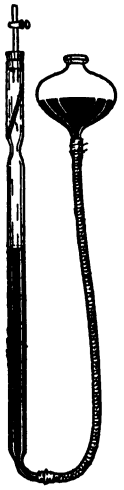


FIG 285.—Effect of pressure on phosphorescence in oxygen.

A stick of phosphorus is placed in the constricted part of a tube containing oxygen confined over mercury, the levelling tube being adjusted so that the gas is at atmospheric pressure (Fig. 285). 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 27°, the glow is very bright at 36°, and the phosphorus then very easily inflames. The following experiment is more convenient, as there is then no danger of the phosphorus taking fire

EXPT. 9.—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. Shake the liquid round the inside of the flask. On reducing the pressure of the oxygen the glow commences again suddenly.

Graham (1829) found that the glow is inhibited by 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.

Schonbein (1848) considered that the glow is intimately related to the formation of *ozone*, 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 also an indifferent gas (N_2 or H_2) when passed over phosphorus glows when mixed with oxygen In a rapid stream of air, the glow is detached from the solid phosphorus.

Hydrogen phosphides.—Phosphorus forms two important hydrogen compounds:

PH_3, **Trihydrogen phosphide** (*gaseous phosphoretted hydrogen*; *phosphine*), m. pt. −132·5°, b pt. −87·4°.

P_2H_4, **Dihydrogen phosphide** (*liquid phosphoretted hydrogen*), b. pt. 58° (735 mm.).

Two doubtful solid hydrogen phosphides, $P_{12}H_6$ and P_9H_2, have also been described.

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 was 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:

$$P_4 + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

The hypophosphite is 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 $2P + 2NaOH + 2H_2O = 2NaH_2PO_2 + H_2$. Over 60 per cent. of hydrogen may be present in the gas

EXPT. 10.—A few pieces of white phosphorus are placed in a flask (Fig. 286) containing a 30–40 per cent. solution of caustic soda The air is swept out by a current of hydrogen, to avoid the explosion which would occur by the spontaneous ignition of a mixture of phosphine and air, and the flask is heated to a fairly high temperature. 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

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.

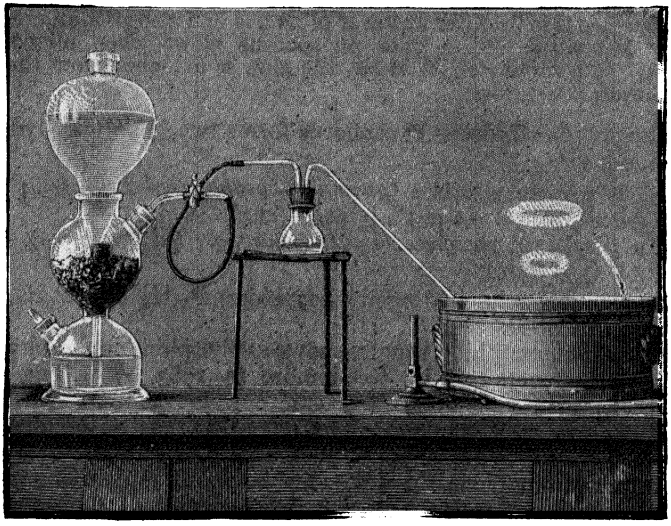


FIG. 286.—Preparation of phosphine.

The spontaneous inflammability of the gas prepared by Gengembre's method is due to the presence of traces of the vapour of the liquid hydride: $6P + 4NaOH + 4H_2O = 4NaH_2PO_2 + P_2H_4$.

A spontaneously inflammable gas is obtained by the action of water on crude calcium phosphide: $Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$.

Davy showed that pure 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 in air at about 150°: $4H_3PO_3 = 3H_3PO_4 + PH_3$.

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 also prepared 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):

$$2AlP + 3H_2SO_4 = Al_2(SO_4)_3 + 2PH_3.$$

The normal density of phosphine is 1·5293 gm /lit. It is sparingly soluble in water, alcohol, or ether. It is decomposed by electric sparks, depositing red phosphorus and increasing in volume in the ratio of three to two: $2PH_3 = 2P + 3H_2$. In this way its composition is determined. The gas is also decomposed by heating at 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 air or oxygen is not spontaneously explosive, but if the pressure is reduced a violent explosion occurs (Labillardière, 1817).

A mixture of phosphine with 3 vols. of nitric oxide or 2 vols. of nitrous oxide explodes when sparked:

$$2PH_3 + 8N_2O = P_2O_5 + 3H_2O + 8N_2$$

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, or the metals with phosphorus, or the phosphates with carbon in the electric furnace.

EXPT 11.—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 is neutral to litmus paper it is capable of acting as a feeble base, forming **phosphonium salts** with dry 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, formed on mixing PH_3 and HI gas at the ordinary temperature and pressure. It dissociates at 30°, but the crystals can be sublimed. Phosphonium iodide is at once decomposed by water or alkalies, evolving pure phosphine: $PH_4I + Aq. = PH_3 + HIAq$. It is most conveniently prepared by the following process.

EXPT. 12.—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 175 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

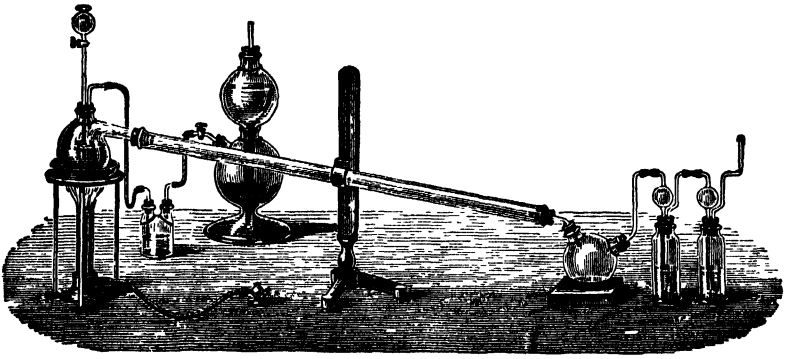


FIG 287.—Preparation of phosphonium iodide

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. 287) 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

$$9P + 5I + 16H_2O = 4H_3PO_4 + 5PH_4I.$$

Liquid hydrogen phosphide.—This substance is obtained together with phosphine and a solid hydrogen phosphide (or perhaps amorphous phosphorus) by the action of water on crude calcium phosphide: $Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + P_2H_4 + H_2$.

Calcium phosphide, Ca_3P_2, is formed as a reddish-brown solid containing pyrophosphate, $Ca_2P_2O_7$, by passing phosphorus vapour over fragments of quicklime heated to dull redness, or in a pure state by heating calcium and phosphorus together under petroleum.

EXPT. 13.—If pieces of calcium phosphide are dropped into warm water in a beaker and covered with a funnel, gaseous phosphoretted hydrogen 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 hydrogen phosphide, pieces of calcium phosphide are dropped through a wide tube into water at 60° in a Woulfe's bottle (Fig. 288), the air having been previously displaced by hydrogen The gas is passed through a cooled tube to deposit moisture, and the liquid hydrogen phosphide then condensed in a second tube cooled in a freezing mixture.

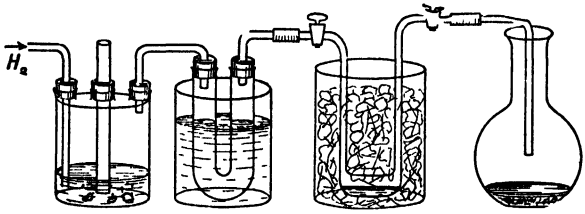


FIG. 288.—Preparation of liquid hydrogen phosphide.

The empirical formula of liquid hydrogen phosphide is PH_2; the formula P_2H_4 is given to the substance by analogy with hydrazine, N_2H_4, and the vapour density corresponds approximately with this, but the vapour is unstable. The liquid decomposes on exposure to light; gaseous phosphine is evolved, and yellow 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.—The yellow 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. The identity of all these solids is not beyond doubt.

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 said to be 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 iodides are PI_3 and P_2I_4.

PF_3, colourless gas, b. pt. $-95°$, m. pt. $-160°$.

PF_5, colourless gas, b pt. $-75°$, 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 $-40°$.

PBr_5, yellow crystalline solid, b. pt. 106°, decomposes on heating.

PI_3, dark red crystals, m. pt. 61°.

P_2I_4, orange-red crystals, m pt 110°.

The compounds PBr_7, PBr_2F_3, $PCl_3Br_2 \cdot Br_2$, etc , are also known. *E.g* , $2PCl_3 + Br_2 = PCl_4Br + PCl_2Br$.

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 mixture of PF_3 with oxygen explodes on sparking, POF_3 being formed. The **pentafluoride,** PF_5, is formed when phosphorus burns in fluorine ; when arsenic trifluoride is added to phosphorus pentachloride in a freezing mixture · $3PCl_5 + 5AsF_3 = 3PF_5 + 5AsCl_3$, when phosphorus fluorbromide (obtained by cooling a mixture of bromine and PF_3 to $-20°$) is warmed to 15° : $5PF_3Br_2 = 3PF_5 + 2PBr_5$, or by heating 25 gm. of P_2O_5 and 55 gm. of CaF_2 in an iron tube 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 $2PF_5,5NH_3$. **Phosphorous oxyfluoride,** POF_3, is obtained by heating cryolite with P_2O_5 in a brass tube , it is a gas, b. pt $-40°$, m. pt $-68°$, collected over mercury. It is also formed by the action of dry HF on P_2O_5, or ZnF_2 on $POCl_3$.

Phosphorus trichloride, PCl_3 (Gay-Lussac and Thenard, 1808) 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. 249). 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). It forms with ammonia a white compound $PCl_3,5NH_3$. Sulphur trioxide reacts violently with phosphorus trichloride : $SO_3 + PCl_3 = SO_2 + POCl_3$.

EXPT. 14.—31 gm. of white phosphorus is cut under water into pieces which will pass through the tubulure of a retort; these are dried between filter paper one at a time and inserted by means of crucible tongs into the dry retort previously filled with carbon dioxide A good cork carrying a leading-in tube which can be moved, is inserted into the tubulure of the retort, and the tube attached by rubber tubing to the drying tube of the chlorine apparatus Chlorine is now passed in, the retort not being heated The phosphorus burns with a pale flame forming PCl_3, which distils over. The stream of chlorine must pass rapidly and steadily; if a white sublimate forms (PCl_5) lower the inlet tube nearer the phosphorus, whilst if a yellowish-red sublimate forms in the retort, raise the inlet tube.

Phosphorus pentachloride, PCl_5 (Davy, 1810; Dulong, 1816) is prepared by dropping the trichloride into dry chlorine or by burning phosphorus in excess of chlorine. It is a white solid, which sublimes at the ordinary pressure below 100° without previous fusion, the vapour being dissociated into trichloride and chlorine: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. 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: $PCl_5 + Zn = ZnCl_2 + PCl_3$.

EXPT. 15 —Allow PCl_3 to drop slowly into a dry flask cooled in ice, through which a current of dry chlorine is passed A white powder of PCl_5 collects in the flask (Fig. 289).

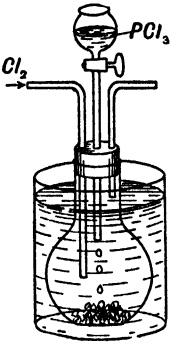


FIG 289.—Preparation of phosphorus pentachloride.

Phosphorus tri- and penta-chlorides are violently hydrolysed by water, the reactions being irreversible. 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 (Wurtz, 1847), 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 at once to the pentachloride, phosphoric acid is produced: $PCl_5 + 4H_2O = 5HCl + H_3PO_4$.

Inorganic oxy-acids, organic acids (containing the carboxyl group —CO·OH), and alcohols (hydroxides of hydrocarbon radicals, *e.g.*, methyl alcohol, CH_3·OH) containing the hydroxyl group OH, react with phosphorus pentachloride, the hydroxyl group being eliminated and substituted by an atom of chlorine:

$$SO_2(OH)_2 + PCl_5 = SO_2Cl_2 + POCl_3 + 2HCl.$$

Phosphorus pentachloride reacts with dry ammonia forming a white solid mixture of substances, converted by water into **phosphamide**, $PO(NH)NH_2$, a white insoluble powder If the product of the action of NH_3 on PCl_5 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°, ammonium chloride 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°. Ether solutions of these compounds when shaken with water form **metaphosphimic acids**, stable salts of which, *e g*, $P_3N_3O_6H_3(NH_4)_3 + H_2O$, are known.

Phosphoryl nitride, PON, is a white powder formed by heating to redness the solid product of the interaction at 0° of ammonia gas and phosphoryl chloride.

Phosphorus pentasulphide reacts with dry ammonia, when the product is heated at 230° in ammonia and then at a higher temperature in a current of hydrogen, decomposition occurs and at a bright red heat **phosphorus nitride**, P_3N_5, is left It is a white amorphous powder, decomposing into its elements when heated in a vacuum at a high temperature It is scarcely affected by boiling water but is completely decomposed into ammonia and phosphoric acid by water at 180°. It takes fire when heated in chlorine or oxygen and is decomposed by many metals.

White phosphorus explodes in contact with liquid chlorine and 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 exists in two forms: a yellow variety obtained by rapidly cooling the vapour and a red stable variety obtained on slow cooling. The vapour is dissociated: $PBr_5 \rightleftharpoons PBr_3 + Br_2$. The **heptabromide**, PBr_7, is obtained by heating PBr_5 and bromine in a sealed tube at 90°.

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 formed as an oily fuming liquid, m. pt. $-28°$, by the action of the silent discharge on a mixture of PCl_3 vapour and hydrogen Some is also formed by the action of a zinc arc on PCl_3 (Stock, 1925)

Matches.—Common matches are made by dipping thin strips of wood into a paste which contains phosphorus sulphide (P_4S_3) and potassium chlorate, together with oxides of iron and zinc, ground glass, and glue. The heads ignite when rubbed on sandpaper, the local heating causing combustion to begin " Safety matches " are tipped with a paste containing potassium chlorate, potassium dichromate, manganese dioxide, sulphur, oxide of iron, ground glass, gum and glue. 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 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 or P_8O_{16}	**Hypophosphoric acid**, $H_4P_2O_6$
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.**
	Permonophosphoric acid, H_3PO_5.
	Perdiphosphoric acid, $H_2P_2O_8$.

The so-called **phosphorus sub-oxides**, P_4O and P_2O, are probably impure red phosphorus. **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 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 is converted into red phosphorus.

EXPT. 16.—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 Red phosphorus remains in the capsule.

Phosphorus pentoxide.—This oxide is always prepared by the combustion of phosphorus in air or oxygen. On a large scale, the apparatus shown in Fig. 290 is used.

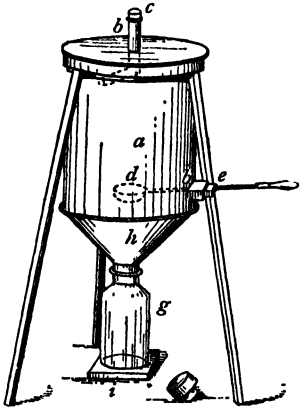


FIG. 290.—Preparation of phosphorus pentoxide

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 air is allowed to enter between the iron funnel *h* and the cylinder by removing *i*. Commercial phosphorus pentoxide contains some trioxide, P_2O_3, and metaphosphoric acid. It may be purified by volatilising in a current of dry air or oxygen in a hard glass or iron tube, and condensing in a cooled receiver. Lower oxides of phosphorus may be oxidised to P_2O_5 by heating at 175°–220° in a current of ozonised air. The purified product should give no black colour with silver nitrate solution.

The voluminous powder, 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.

The vapour density at 1400° is slightly higher than corresponds with 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 reacts with a hissing noise and the evolution of much heat (*cf.* SO_3, p. 508); flocks of metaphosphoric acid are produced: $P_2O_5 + H_2O = 2HPO_3$. If the solution 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, $H_4P_2O_7$, being formed as an intermediate product. 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: $2HNO_3 \rightleftharpoons N_2O_5 + H_2O$

Orthophosphoric acid.—The natural mineral phosphates and bone-ash are salts of orthophosphoric acid, and the fertiliser *guano*, consisting of the excreta of sea birds, is rich in phosphates and also in combined nitrogen Another source of the phosphate used in fertilisers is the *basic slag* of steel furnaces, containing $Ca_4P_2O_9$. The acid was prepared by Marggraf (the discoverer of beet-sugar) in 1743 from microcosmic salt, and from phosphorus by combustion. He showed that it was not a compound of phlogiston and hydrochloric acid, as taught by Stahl. Marggraf also noticed that the product of the combustion of phosphorus weighed more than the phosphorus but did not explain this result, which was reinvestigated by Lavoisier in 1772–77. Scheele obtained the acid by oxidising phosphorus with nitric acid.

Orthophosphoric acid, H_3PO_4, is prepared technically by digesting bone-ash with diluted sulphuric acid 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, $CaH_2(PO_4)_2$ Phosphoric acid is also made by the electric furnace process (p 604), air being admitted to burn the phosphorus vapour to P_2O_5, and CO to CO_2, water is sprayed into the cooled gas and crude 85 per cent. phosphoric acid separated by electrostatic precipitation (p. 12) The acid may then be purified. Blast furnaces are also used in the process.

Pure orthophosphoric acid is obtained by the oxidation of phosphorus with nitric acid. Oxides of nitrogen are evolved:

$$P_4 + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2.$$

EXPT. 17.—Place 112 c c. of concentrated nitric acid and 183 c.c. of water in a 2 litre R.B. flask fitted with a ground-in reflux condenser. Add 31 gm of red phosphorus in portions of one-fifth at a time to the acid, warming till red vapours appear and cooling if the reaction is too

violent. When all the phosphorus is dissolved (neglect any black residue), add 20 c c of strong nitric acid and heat in a porcelain dish to oxidise phosphorous acid When all reaction ceases and a little of the liquid diluted with water gives no black precipitate with $AgNO_3$, due to H_3PO_3, add an equal volume of water and filter if necessary. Evaporate in a porcelain dish over a small flame till a thermometer in the liquid rises just to 180° Cool in a small dish in a vacuum desiccator over concentrated sulphuric acid, placing the desiccator in a freezing mixture deliquescent crystals of orthophosphoric acid, H_3PO_4, are slowly deposited If the temperature is carried beyond 180° in the evaporation some metaphosphoric acid is formed, and crystallisation will not occur.

The crystals of orthophosphoric acid melt at 38·6°–42·3°, 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 precipitated as ferric phosphate and is removed from the solution :

$$3Ca(C_2H_3O_2)_2 + 2H_3PO_4 + 2FeCl_3 = 2FePO_4 + 3CaCl_2 + 6C_2H_4O_2.$$

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, which are precipitated as phosphates.

The soluble primary phosphates in solution are acid to litmus; tertiary phosphates are alkaline; secondary phosphates are faintly alkaline—practically neutral:

$$H_2PO_4'' \rightleftharpoons HPO_4'' + H^{\cdot}.$$
$$PO_4''' + H^{\cdot} + OH' \rightleftharpoons HPO_4'' + OH'.$$
$$HPO_4'' + H + OH' \rightleftharpoons H_2PO_4' + OH'.$$

The first hydrogen in orthophosphoric acid is easily ionised, the second with difficulty, and the third only in presence of excess of base.

$$H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4' \rightleftharpoons 2H^{\cdot} + HPO_4'' \rightleftharpoons 3H^{\cdot} + PO_4'''.$$

On titration with litmus, phosphoric acid 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 *ortho*-phosphates when treated with excess of nitric acid and a solution of ammonium molybdate slowly deposit *in the cold* a canary-yellow precipitate of **ammonium phosphomolybdate,** readily soluble in ammonia.

Pyro- and meta-phosphates do not give this reaction unless the solution is heated, or allowed to stand for a long time, when they are converted into orthophosphoric acid. Arsenic acid, H_3AsO_4, gives a similar precipitate, but *only on heating*. The precipitation of orthophosphoric acid also occurs much more rapidly at 60°–65°.

Ordinary **sodium phosphate,** $Na_2HPO_4,12H_2O$, prepared by neutralising phosphoric acid with caustic soda or sodium carbonate (the end-point should be faintly alkaline) and evaporating, forms efflorescent monoclinic crystals, m. pt. 35°, readily soluble in water. The effloresced salt contains $7H_2O$.

Microcosmic salt, or sodium ammonium hydrogen phosphate, $NaNH_4HPO_4,4H_2O$, is formed 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 as orthorhombic crystals 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 sodium phosphate and excess of caustic soda in hot water and evaporating; hexagonal crystals of $Na_3PO_4,12H_2O$ separate, not efflorescent or deliquescent. It 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.—This acid is slowly formed (with a little metaphosphoric acid) when orthophosphoric acid is heated at 213° (rapidly above 240°): $2H_3PO_4 = H_4P_2O_7 + H_2O$. If ordinary sodium phosphate is heated above 240°, it loses 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 hydrogen sulphide, gives a black precipitate of lead sulphide and a solution of pyrophosphoric acid: $Pb_2P_2O_7 + 2H_2S = 2PbS + H_4P_2O_7$. Pure pyrophosphoric acid is obtained by gently heating a mixture of crystals of orthophosphoric acid and phosphorus oxychloride: $5H_3PO_4 + POCl_3 = 3H_4P_2O_7 + 3HCl$. The product is evaporated *in vacuo*, and on cooling to −10° for some time yields white granular crystals of pyrophosphoric acid, $H_4P_2O_7$, m. pt. 61°.

When a solution of orthophosphoric acid or an orthophosphate mixed with ammonium chloride is made alkaline with ammonia and magnesium chloride or sulphate 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, or by shaking violently in a stoppered bottle. When washed with dilute ammonia, dried, and heated to dull 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 similarly 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 common, 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); $Ag_4P_2O_7$ (insoluble); $Ag_2H_2P_2O_7$ (soluble); $Na_3HP_2O_7$ and $NaH_3P_2O_7$ are also known. Complex ions containing metals (Zn, Pb, Ag, etc.) are formed by dissolving the insoluble pyrophosphates in sodium pyrophosphate solution.

Metaphosphoric acid.—This acid is formed when either ortho- or pyrophosphoric acid is heated at 316° (best in a gold crucible): $H_3PO_4 = HPO_3 + H_2O$ (Graham, 1833). It is a sticky mass. By

prolonged heating to redness, 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 formula, HPO_3 Metaphosphoric acid is also formed on heating ammonium phosphate: $(NH_4)_3PO_4 = HPO_3 + 3NH_3 + H_2O$.

According to Geuther, pure metaphosphoric acid is best obtained from the ortho- or pyro- acid and phosphorus oxychloride according to the reactions

$$2H_3PO_4 + POCl_3 = 3HPO_3 + 3HCl,$$
$$2H_4P_2O_7 + POCl_3 = 5HPO_3 + 3HCl.$$

Sodium metaphosphate is formed as a clear glass when microcosmic salt, acid sodium orthophosphate, or acid sodium pyrophosphate is heated to redness :

$$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O ;$$
$$NaH_2PO_4 = NaPO_3 + H_2O$$

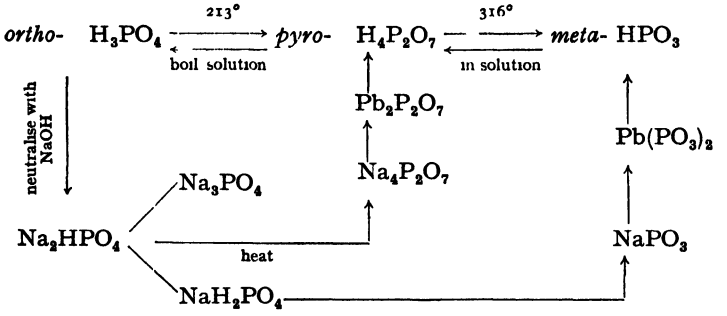
If a little microcosmic salt is heated on a loop of platinum wire a fused bead of $NaPO_3$ remains, which dissolves many metallic oxides with the formation of orthophosphates possessing characteristic colours (" microcosmic bead ") . $CoO + NaPO_3 = CoNaPO_4$ (blue).

A nearly neutralised solution of a metaphosphate gives a white *gelatinous* precipitate of **silver metaphosphate**, $AgPO_3$, with silver nitrate.

Metaphosphoric acid, unlike the other phosphoric acids, at once coagulates albumin (white of egg), and gives a white precipitate with barium chloride in acid solution.

The metaphosphates are much more numerous than the simple formula of the acid HPO_3 would indicate, and both polymeric and metameric varieties 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. 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 are summarised in the following diagram.



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 aP_2O_5, bP_2O_5, and cP_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 example, 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

Perphosphoric Acids.—Phosphates may crystallise with hydrogen peroxide of crystallisation: those with an acid reaction, such as primary phosphates (NaH_2PO_4, etc.), either do not react or form very unstable compounds; tertiary phosphates, with an alkaline reaction (K_3PO_4, etc.) decompose hydrogen peroxide. The secondary phosphates and pyrophosphates of alkali metals give fairly stable crystalline compounds, *e.g.*, $K_2HPO_4,2\frac{1}{2}H_2O_2$; $K_4P_2O_7,3H_2O_2$; $CaHPO_4,\frac{1}{2}H_2O_2$; $(NH_4)_2H_2P_2O_7,H_2O_2,2H_2O$. None of these compounds is a true perphosphate. True perphosphates, which do not give any of the reactions of hydrogen peroxide, are obtained in solution by the electrolysis of secondary phosphates of potassium, rubidium, caesium and ammonium

in presence of fluorides and chromates, but not from lithium or sodium salts. They oxidise acidified manganous salt solutions to pink permanganic acid and give a black precipitate with silver nitrate solution. These are salts of **perdiphosphoric acid**, $H_4P_2O_8$, and **permonophosphoric acid**, H_3PO_5, (Husain and Partington, 1928).

Phosphorus oxychloride.—When phosphorus pentachloride is treated with small quantities of water until the solid is completely liquefied, a colourless fuming liquid, b. pt 107·2°, m. pt. 1·38°, is formed which has the composition $POCl_3$ and is known as phosphorus oxychloride : $PCl_5 + H_2O = POCl_3 + 2HCl$. It is the chloride of orthophosphoric acid and is also formed by the direct oxidation of phosphorous 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 : $P_2O_5 + 3PCl_5 = 5POCl_3$.

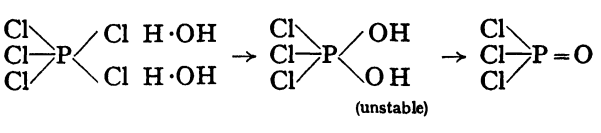
The formation of the oxychloride by the action of phosphorus pentachloride on compounds containing hydroxyl groups has already been described ; the action on oxalic and boric acids is interesting, since in the first case the by-products are gaseous and are evolved, leaving the phosphorus oxychloride, and in the second case the by-product is non-volatile so that the oxychloride may be distilled off :

$$C_2O_4H_2 + PCl_5 = POCl_3 + CO_2 + CO + 2HCl.$$
$$2H_3BO_3 + 3PCl_5 = B_2O_3 + 3POCl_3 + 6HCl$$

The oxychloride is readily hydrolysed by excess of water, forming orthophosphoric acid : $POCl_3 + 3H_2O = H_3PO_4 + 3HCl$. When treated with water and excess of zinc dust, it gives inflammable phosphine ; PCl_3 does not.

Phosphorus oxybromide, $POBr_3$ (solid, b. pt. 190°), is similarly prepared from the pentabromide.

Constitution of phosphoric acids.—From its method of preparation, phosphorus oxychloride is given the formula $O=P(Cl_3)$:



It contains the tervalent radical **phosphoryl**, $O=P\equiv$, and is more stable than the pentachloride, which may be regarded as containing the radical $Cl_2=P\equiv$, since the pentachloride is decomposed on heating whilst the oxychloride volatilises unchanged.

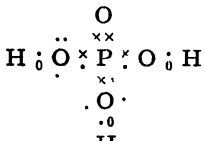
Since orthophosphoric acid is produced by the action of water on phosphorus oxychloride (**phosphoryl chloride**), the acid probably contains the phosphoryl radical ·

$$O=P(Cl)(Cl)(Cl) + 3H\cdot OH \rightarrow O=P(OH)(OH)(OH) + 3HCl.$$

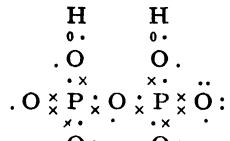
In reactions where ions are not concerned, all three hydroxyl groups of orthophosphoric acid are readily removed, as in the formation of the ethyl ester, $O\,P(OC_2H_5)_3$.

The electronic formulae of the phosphoric acids may be represented as follows, giving the phosphorus a covalency of four ·

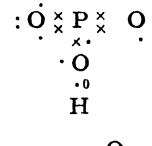
I Orthophosphoric acid

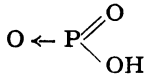


II Pyrophosphoric acid.



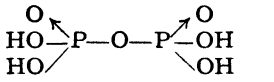
III Metaphosphoric acid



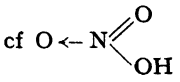


$(HO)_3P\rightarrow O$

also $Cl_3P\rightarrow O$



cf



Phosphorus, unlike nitrogen, may exhibit a covalency of five, as in PF_5, PCl_5, etc., although PCl_5 has been regarded as a salt, $[PCl_4]^+Cl^-$.

Pyrophosphoryl chloride, $P_2O_3Cl_4$, or $O(POCl_2)_2$, 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. 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

Mono-, di- and **hexafluophosphoric acids**, H_2PO_3F, HPO_2F_2 and HPF_6, are obtained by the action of P_2O_5 on 40 per cent HF, and salts are known, *e g*, $NH_4PO_2F_2$ from P_2O_5 and NH_4F at 130°. The PF_6' ion is very stable towards boiling water and alkali hydroxides The monofluophosphates are very similar in properties to the sulphates.

Phosphorus trioxide.—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, was

noticed by Sage (1777), but the pure substance was first isolated by Thorpe and Tutton in 1890. Phosphorus is burnt in a limited supply of air, and the product condensed by cooling.

Sticks of phosphorus 1½ in long were placed in the hard glass tube, *a*, (Fig. 290), 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

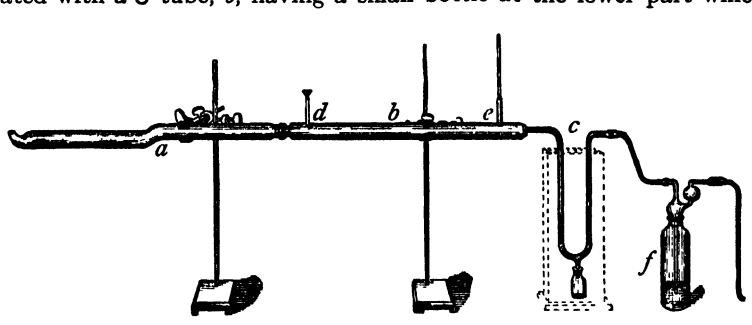


FIG 290 —Preparation of phosphorus trioxide

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. This reaction is the only known method of preparing phosphorus trioxide. Details of the method of preparation are given by Wolf and Schmager (1929).

Phosphorus trioxide is a white waxy crystalline solid, m pt. 23·8°, 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, N_4O_6). Unless quite pure, the trioxide slowly turns red in light owing to the conversion of white phosphorus contained as an impurity into red phosphorus (C. C. Miller, 1929). 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. When pure it does not glow in air. If heated in oxygen it burns ; in chlorine it inflames spontaneously, forming $POCl_3$ and the chloride of metaphosphoric acid, PO_2Cl, or possibly a mixture of $P_2O_3Cl_4$ 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: $P_4O_6 + 6H_2O = PH_3 + 3H_3PO_4$.

Alkalies act similarly. Phosphorus trioxide 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.—When the liquid trioxide is heated in a sealed tube it is stable up to 200°; at 210° it becomes turbid, and at 440° 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°. The vapour density at 1400° corresponds with P_8O_{16}. 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_2O_5, P_4O_6, and red phosphorus. On heating this in a sealed tube at 290°, 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, said to be formed as a reddish-yellow powder by heating phosphorous acid and PCl_3, is impure amorphous phosphorus (Chalk and Partington, 1927)

Phosphorous acid.—Phosphorous acid 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, 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 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.

$$PCl_3 + 3C_2H_2O_4 = H_3PO_3 + 3CO_2 + 3CO + 3HCl.$$

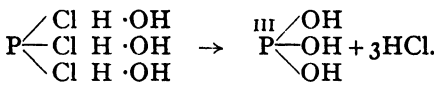
Phosphorous acid forms white crystals, m. pt. 71·7°–73·6°; it is very soluble in water. When heated it decomposes, evolving pure phosphine and leaving orthophosphoric acid: $4H_3PO_3 = 3H_3PO_4 + PH_3$. If the acid is heated in air, the phosphine ignites and burns in bright flashes. This result is obtained by heating the residue left on

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:

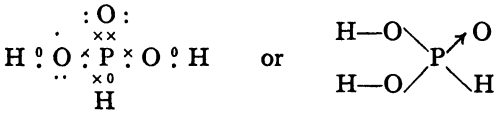
$$2HgCl_2 + H_2O + H_3PO_3 = Hg_2Cl_2 + 2HCl + H_3PO_4.$$

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 ($H_2S_5O_6$ is also formed): $H_2SO_3 + 2H_3PO_3 = 2H_3PO_4 + H_2O + S$; 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 $P(OH)_3$:



Normal esters of phosphorous acid, such as triethyl phosphite, $P(OEt)_3$, are in fact known, but the usual dibasic character of the acid is represented by a different formulation:



the phosphorus thus exhibiting the covalency of four, as in the phosphoric acids. The oxide P_2O_3 has probably a structure like that of N_2O_3 (p. 585).

The reducing properties of the acid 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 do *not* evolve hydrogen (*cf.* hypophosphites). Ordinary **sodium phosphite** is $Na_2HPO_3,5H_2O$. An acid sodium salt, $2NaH_2PO_3,5H_2O$, a calcium salt, $2CaHPO_3,3H_2O$ and an acid calcium salt $CaH_4(PO_3)_2,H_2O$, are known.

Phosphorous acid reacts with phosphorus pentachloride in the normal manner, forming the acid chloride, PCl_3:

$$H_3PO_3 + 3PCl_5 = PCl_3 + 3POCl_3 + 3HCl.$$

The acid H_3PO_3 is **orthophosphorous acid.** **Pyrophosphorous acid,** $H_4P_2O_5$, is formed in needles, m. pt. 38°, by shaking PCl_3 with H_3PO_3 for five hours at 30°–40°, and leaving in a desiccator over KOH and P_2O_5. **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 $2PH_3 + 3O_2 = 2H_3PO_3$.

Hypophosphoric Acid.—If sticks of phosphorus enclosed in glass tubes open at both ends (Fig. 291), are supported in a glass funnel over water under a bell-jar, oxidation occurs with the production of fumes which sink and dissolve in the water. Dulong 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 partly neutralised with soda, sparingly soluble crystals of $Na_2H_2P_2O_6,6H_2O$ slowly separate. If lead nitrate is added to a solution of this salt, $Pb_2P_2O_6$ is precipitated; on suspending this in water and passing hydrogen sulphide, a solution of the free acid, now called hypophosphoric acid, $H_4P_2O_6$ is obtained, which on evaporation in a vacuum desiccator over sulphuric acid gives crystals, $H_4P_2O_6,2H_2O$, which readily lose water, forming $H_4P_2O_6$.

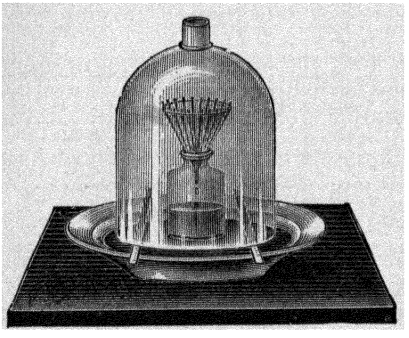


FIG. 291.—Preparation of hypophosphoric acid.

If phosphorus is heated on a water-bath with a solution of copper nitrate, or a solution of silver nitrate containing free nitric acid, copper or silver phosphides, and then salts of hypophosphoric acid are formed. 6 gm. of silver nitrate 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, $Ag_4P_2O_6$, separates; this may be decomposed by hydrochloric acid to obtain hypophosphoric acid. The sodium salt is formed by the action of sodium hypochlorite solution on red phosphorus (Probst, 1929).

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 guanidine salt is sparingly soluble. The formula of the acid is probably $H_4P_2O_6$, or $[(HO)_2{:}P{:}O]{\cdot}O{\cdot}P(OH)_2$, since the molecular weight of the ester in solution corresponds with $(C_2H_5)_4P_2O_6$. The acid salt, $Na_3HP_2O_6,9H_2O$, is known.

Hypophosphoric acid is oxidised by hot potassium permanganate, but in the cold is only slowly oxidised. The oxide P_2O_4 with water produces

only a mixture of phosphoric and phosphorous acids · it is probably not the true anhydride of hypophosphoric acid. It may be regarded as phosphoryl metaphosphate, $O=P-O-P\overset{O}{=}O$

Hypophosphorous acid.—The residue from the preparation of phosphine from phosphorus and alkali contains a salt of hypophosphorous acid, H_3PO_2 (Dulong, 1816). The barium salt 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, the excess of baryta removed by carbon dioxide, the barium hypophosphite, $Ba(H_2PO_2)_2$, H_2O, is recrystallised, and a solution of it is decomposed with the calculated amount of sulphuric acid .

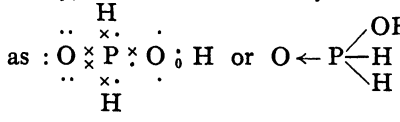
$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2.$$

The filtrate is carefully evaporated below 130° to a syrup, cooled to 0° in a desiccator over P_2O_5 and KOH, and crystallised. A 10 per cent. solution of the acid is prepared commercially

Hypophosphorous acid melts at 17·4°–26·5° ; on heating it decomposes at 130°, becoming yellow and evolving phosphine : $2H_3PO_2 = H_3PO_4 + PH_3$. The salts also evolve phosphine on heating :

$$4NaH_2PO_2 = 2PH_3 + 2Na_2HPO_4.$$

The acid and its salts may be titrated with permanganate after addition of sulphuric acid . $H_3PO_2 + 2O = H_3PO_4$.

Hypophosphorous acid and its salts are powerful reducing agents, precipitating metals from solutions of their salts. 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,** $Ca(H_2PO_2)_2$, prepared by heating phosphorus with caustic soda or milk of lime, respectively, and used medicinally as tonics. The acid may be formulated as  , which shows that it is monobasic.

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.

Sulphides of phosphorus.—White phosphorus and sulphur react with explosive violence 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. A sulphide P_3S_6 has also been described. The pure **pentasulphide** is a pale yellow solid melting at 290° and boiling at 513°-515°; the vapour has the normal density. The substance is rapidly hydrolysed by water:

$$P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S.$$

It can be purified by recrystallising from carbon disulphide and heating at 150° in carbon dioxide to remove the solvent. **Tetraphosphorus trisulphide**, P_4S_3, is purified by crystallisation from carbon disulphide or by distillation *in vacuo*. It is bright yellow, 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, sparingly soluble in CS_2, m. pt. 310°, b. pt. 523°.

Thiophosphoric acids.—Sodium salts of **monothiophosphoric acid**, H_3PSO_3, **dithiophosphoric acid**, $H_3PS_2O_2$, and **trithiophosphoric acid**, H_3PS_3O, are formed 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 the reaction· $P_2S_5 + 3PCl_5 = 5PSCl_3$. It is hydrolysed by water $PSCl_3 + 4H_2O = H_2S + 3HCl + H_3PO_4$. **Thiophosphoryl fluoride**, PSF_3, is a colourless spontaneously inflammable gas, obtained by the reaction· $P_2S_5 + 3PbF_2 = 3PbS + 2PSF_3$

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.

CHAPTER XXXIII

ARSENIC

Arsenic.—The minerals *realgar* (red), As_2S_2, and *orpiment* (yellow), As_2S_3, were known to the ancients but confused with cinnabar (HgS) under the name *sandaraké*, or *arsenikon*. Olympiodoros (fifth century) describes *white arsenic* (arsenious oxide, As_2O_3) obtained by roasting the sulphides in air, as "white alum" The element 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 The composition of white arsenic, as the calx of "metallic" arsenic, was recognised by Brandt in 1733.

The chief minerals containing arsenic are the sulphides, *orpiment* (As_2S_3) and *realgar* (As_2S_2); the oxide, *arsenolite*, As_2O_3; *arsenical iron*, $FeAs_2$; *arsenical nickel*, NiAs; *nickel glance*, NiAsS, *tin-white cobalt*, (Co,Ni,Fe)As_2; *arsenical pyrites*, or *mispickel*, FeAsS, or Fe_2AsS_2; *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 *mimetesite*, $3Pb_3(AsO_4)_2,PbCl_2$. The free element is also found.

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 and coal smoke, especially in yellow fogs, may contain arsenious oxide from the pyrites in the coal. Traces of arsenic occur in some mineral waters, in the human body, and most foods.

In *roasting* minerals in a current of air for metallurgical treatment, fumes of impure **arsenious oxide**, As_2O_3 are often evolved, and may be condensed in flues as a 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 in a current of air.

A suitable apparatus is the **revolving calciner** of Oxland and Hocking (Fig. 292), 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.

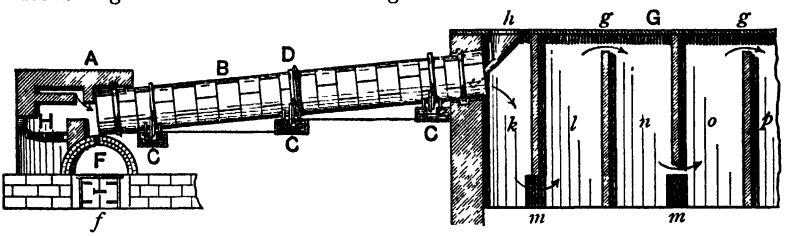


FIG 292 —Oxland and Hocking's revolving calciner.

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. Arsenious oxide is used as a poison for vermin, for weed-killer, in taxidermy for preserving skins, in glass-making for removing colour from the glass, and in minute amounts medicinally as a tonic and in skin and other diseases.

Arsenic.—The element arsenic, which occurs native, 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 : $As_2O_3 + 3C = 3CO + 2As$. It is also prepared 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 : $FeAsS = FeS + As$, which is purified by resublimation from charcoal powder. Arsenic sulphides are *not* reduced by heating with charcoal ; with potassium cyanide they give arsenic.

EXPT 1 —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, the element arsenic exists in different allotropic forms.

The following modifications of arsenic have been described :

(1) α-**Arsenic,** or **yellow arsenic** corresponding with white 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 colourless vapour the density of which varies with the temperature, indicating dissociation: $As_4 \rightleftharpoons 2As_2$. (Theoretical: As_4 150, As_2 75)

Temperature	860°	1714°	1736°
Δ (H = 1)	147	79	77

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 814°.

Grey arsenic is not oxidised in dry air, but in presence of moisture rapidly becomes covered with a blackish-grey film containing the trioxide. This can be removed by heating with a little iodine. When heated to 200° in air it shows a distinct phosphorescence, at 400° it burns in air with a white flame. It burns brilliantly in oxygen: $As_4 + 3O_2 = 2As_2O_3$.

EXPT. 2.—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. 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. Dilute nitric acid has little action in the cold; the hot dilute acid slowly oxidises arsenic to arsenious oxide; with concentrated nitric acid, or *aqua regia*, it is rapidly oxidised, **arsenic acid**, H_3AsO_4 (and with *aqua regia* some trichloride, $AsCl_3$) being formed. 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 trioxide. Arsenic is insoluble in aqueous alkalies, but is attacked by fused alkalies forming arsenites and hydrogen: $2As + 6NaOH = 2Na_3AsO_3 + 3H_2$. At high temperatures, some arsenate, Na_3AsO_4, and arsenide, Na_3As, are formed: $4Na_3AsO_3 = 3Na_3AsO_4 + Na_3As$.

β-Arsenic, or **black arsenic** is formed when grey arsenic is rapidly heated in a glass tube in a current of hydrogen, when it 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 apparently 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

Yellow arsenic, or **α-arsenic**, a peculiar allotropic form resembling white phosphorus, is produced by rapidly cooling arsenic vapour. Arsenic is distilled in a current of carbon dioxide; the gases are passed into a U-tube where they meet a current of cooled carbon dioxide, and 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 white 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

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

Hydrogen arsenide.—The only hydrogen compound of arsenic definitely known is AsH_3, arsine, or arseniuretted hydrogen, a colourless gas, b. pt. −54·8°, m pt. −113·5°. It is not formed by direct combination of the elements, but is produced (Proust, 1799) 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 lilac flame Scheele first obtained arsine in 1775 by the action of arsenic acid on zinc. It is 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 the pure gas is evolved on warming.

Pure arsine may also be prepared by the action of dilute hydrochloric acid on zinc arsenide, Zn_3As_2, obtained by heating equal weights of arsenic and zinc in a closed 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 last reaction may become violent. The gas is poisonous. 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 black shining arsenic; a little yellow arsenic is also usually formed. When quite pure and dry the gas is stable. Arsine is decomposed by heat into its elements, the reaction commencing at about 230° $2AsH_3 = 2As + 3H_2$ From the ratio of the volumes of arsine and hydrogen 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 gaseous arsine and its ready decomposition by heat are applied in the very delicate Marsh-Berzelius test

EXPT. 3.—Hydrogen generated in a flask from pure (electrolytic) zinc and pure dilute sulphuric acid is freed from traces of hydrogen sulphide 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. 293). 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 *dilute* solution of arsenious oxide, or any material to be tested for arsenic, be 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

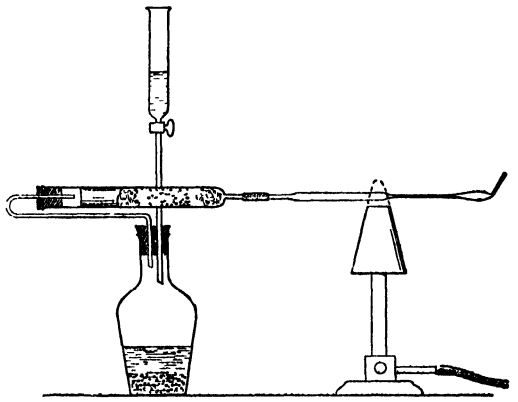


FIG. 293.—Marsh-Berzelius test for arsenic

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. Some varieties of zinc do not easily reduce arsenic compounds, but they may be rendered active by adding a little soluble cadmium salt to the solution in the flask

If the tube is not heated but the gas kindled at the jet, the flame, which is tinged lilac, 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).

Arsine passed into dilute silver nitrate solution gives a black precipitate of metallic silver, and the filtrate contains arsenious acid (*cf.* antimony):

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 6Ag.$$

If the silver nitrate solution is more concentrated, no precipitate is formed but a yellow solution of a double compound of silver arsenide and nitrate is obtained:

$$AsH_3 + 6AgNO_3 = Ag_3As,3AgNO_3 + 3HNO_3.$$

On dilution with water, a black precipitate of silver is deposited:

$$Ag_3As,3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3AsO_3$$

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 sensitive **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.

Ill-defined brown or red **solid hydrides** are 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° they are converted into grey arsenic. They have been given the formulae As_4H_2, AsH_2, and AsH. 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: $As_2O_3 + 6HF \rightleftharpoons 2AsF_3 + 3H_2O$. The water produced in the reaction is retained by the sulphuric acid, otherwise hydrolysis of the fluoride would occur. **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—by heating arsenic with mercuric chloride, by heating arsenious oxide in chlorine, or by distilling a mixture of white arsenic, common salt and concentrated sulphuric acid in a retort, and condensing the vapour in a cooled receiver: $As_2O_3 + 6HCl \rightleftharpoons 2AsCl_3 + 3H_2O$. The distillate is freed from excess of chlorine by distillation over powdered arsenic. The most convenient method of preparation is to treat arsenious oxide with sulphur chloride under a reflux condenser, pass chlorine through the mixture, and distil (Partington, 1929):

$$4As_2O_3 + 3S_2Cl_2 + 9Cl_2 = 8AsCl_3 + 6SO_2.$$

Arsenic trichloride is a colourless oily liquid, b. pt 130·2°, in a freezing mixture it forms pearly crystals, m. pt. −13°. The liquid, sp. gr. 2·2, fumes in moist air and is hydrolysed by water: the first product is a crystalline **hydroxychloride,** but with excess of water arsenious oxide is formed:

$$AsCl_3 + 2H_2O = 2HCl + AsCl(OH)_2;$$
$$2AsCl(OH)_2 + 2H_2O = As_2O_3 + 3H_2O + 2HCl.$$

The hydrolysis is reversible to some extent, showing that arsenic has slight metallic properties; if arsenious oxide is dissolved in fairly concentrated hydrochloric acid and the liquid boiled, arsenious chloride distils over with the steam: $As_2O_3 + 6HCl \rightleftharpoons 2AsCl_3 + 3H_2O$

Arsenic tribromide, $AsBr_3$, is a white crystalline solid, m. pt 31°, b pt. 221°, less easily hydrolysed than $AsCl_3$; **arsenic tri-iodide** forms red hexagonal crystals, m. pt 146°, both compounds are formed by heating arsenic with a solution of the halogen in carbon disulphide. The tri-iodide is hydrolysed only slightly 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, obtained as a dark red mass by heating iodine with arsenic in a closed tube at 260°, is soluble in

carbon disulphide, but is decomposed by water into AsI_3 and arsenic. By heating AsI_3 with iodine at 150° a brown **pentaiodide**, AsI_5, is said to be formed. A **mono-iodide**, AsI, is produced as a brown powder when an alcoholic solution of iodine is saturated with arsine.

Arsenious oxide.—Arsenious oxide or arsenic trioxide, the most important compound of arsenic (known in commerce as "white arsenic," or simply as "arsenic") was known to the ancients and used as a caustic. Its intensely poisonous properties were 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) **amorphous**, sp. gr. 3·738, m. pt 200°; (2) **octahedral**, sp. gr. 3·689, m. pt 275°, which easily sublimes without fusion; (3) **monoclinic**, sp. gr 3·85, m. pt. *c.* 315°, occurring as the mineral *claudetite*.

The vapour density between 570° and 1560° corresponds with As_4O_6; at 1770° with As_2O_3 In solution in nitrobenzene the formula is 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; according to Rushton and Daniels (1926) at 275°–315°. It may be preserved in sealed tubes, but at 100° or in presence of moisture it becomes opaque, and very slowly 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 13°, or in 12 parts 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 (very contradictory figures are quoted), but exceedingly slowly.

The octahedral form, stable under ordinary conditions, 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 monoclinic variety is formed by crystallisation from a boiling saturated solution of the amorphous substance in caustic potash or by sublimation under special conditions.

If arsenious oxide is heated in a sealed tube at 400°, the vitreous form remains at the bottom of the tube, the monoclinic form sublimes to the intermediate part at 200°, and the octahedral form sublimes to the top of the tube. The different crystalline forms may be recognised under the microscope. The transition point of the octahedral and

monoclinic varieties is 250°, but the change is very slow (Rushton and Daniels).

Arsenious oxide is easily *oxidised* to arsenic pentoxide, As_2O_5, arsenic acid or an arsenate, by means of ozone, hydrogen peroxide, chlorine, *aqua regia*, bromine, iodine, nitric acid, and hypochlorites (especially in alkaline solution): *e g*, $As_2O_3 + 2Cl_2 + 2H_2O = As_2O_5 + 4HCl$. It precipitates red cuprous oxide from Fehling's solution.

Arsenious oxide is easily *reduced* to arsenic by heating with charcoal or potassium cyanide, 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:

$$As_2O_3 + 6HCl + 6Cu = 2As + 6CuCl + 3H_2O.$$

If the copper foil is washed, dried, and heated in a tube, a crystalline sublimate of arsenious oxide is formed (**Reinsch's test**). The mere change of colour of the copper is not decisive.

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, decomposed by water, are said to be formed · As_2O_3 then acts as a feebly basic oxide.

Small quantities of arsenious oxide occur in some mineral waters, which are used as nerve tonics and in improving the blood It 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 said to be able to consume arsenious oxide in amounts (0 3 gm) which would ordinarily be fatal. 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 ferric chloride, absorbs arsenious oxide and is recommended as an antidote in cases of poisoning

Arsenious acid.—A solution of arsenious oxide in water has a feebly acid reaction and may contain 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 hydrogen sulphide.

The finely-powdered oxide is not easily wetted by water but a solution can be prepared by boiling. It 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, which oxidises 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 hypothetical acids :

Ortho-arsenious acid, H_3AsO_3; *e.g.*, K_3AsO_3, Ag_3AsO_3, $Pb_3(AsO_3)_2$, $Ca_3(AsO_3)_2$.

Pyro-arsenious acid, $H_4As_2O_5$; *e.g.*, $Ca_2As_2O_5$

Meta-arsenious acid, $HAsO_2$; *e.g.*, $KAsO_2$, $Ba(AsO_2)_2$, $KH(AsO_2)_2$.

If arsenic trioxide is heated with a solution of caustic alkali, arsenites are formed, *e.g.*, Na_3AsO_3, an amorphous powder soluble in and hydrolysed by water. A solution of an arsenite 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 sodium arsenite solution gives a bright green precipitate known as **Scheele's green**, used as an insecticide. This may be $CuHAsO_3$ or $Cu_3(AsO_3)_2,2H_2O$, *i.e.*, cupric arsenite. When dissolved in alkali and boiled, an arsenate is formed and cuprous oxide precipitated: $2Cu^{\cdot\cdot} + AsO_3''' + 4OH' = Cu_2O + AsO_4''' + 2H_2O$. The brilliant pigment **Schweinfürter green**, or **Paris green**, used as an insecticide, has the composition $Cu(C_2H_3O_2)_2,3Cu(AsO_2)_2$, and 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°, or by passing chlorine over the heated trioxide

Arsenic pentoxide and arsenic acids.—Unlike phosphorus, arsenic on combustion in oxygen yields the trioxide, not the pentoxide The trioxide may be converted into pentoxide, As_2O_5, by oxidising agents. Although Cavendish investigated arsenic acid in 1764 he did not publish the results. It was obtained by Scheele (1775) by oxidising the trioxide with chlorine, but is usually prepared by boiling the trioxide with concentrated nitric acid or *aqua regia* and is formed on heating the residue from the preparation of nitrous anhydride :

$$As_2O_3 + 2HNO_3 = As_2O_5 + H_2O + N_2O_3.$$

The very concentrated solution on cooling deposits rhombic crystals of **orthoarsenic acid**, $2H_3AsO_4,H_2O$ (sometimes H_3AsO_4 separates). At 100° these melt, lose water and leave a crystalline powder of $H_5As_3O_{10}$, or $3As_2O_5,5H_2O$. At 160° the acid slowly, or at 200° rapidly, forms arsenic pentoxide, As_2O_5, as a deliquescent white amorphous solid, which dissolves slowly in water. **Pyroarsenic acid**, $H_4P_2O_7$, is obtained in crystals by evaporating a solution of arsenic acid in an open dish until the temperature rises to 170°-180°. Meta-arsenic acid is

not known. Arsenic pentoxide melts at a red heat and evolves oxygen : $As_2O_5 = As_2O_3 + O_2$.

The **arsenates** are isomorphous with the phosphates and probably have similar constitutional formulae The normal orthoarsenates exist as solids and in solution, but the pyro- and meta-arsenates exist only as solids and are prepared by heating the acid and di-acid ortho-salts, as in the case of phosphates :

$$2Na_2HAsO_4 = Na_4As_2O_7 + H_2O ;$$
$$NaH_2AsO_4 = NaAsO_3 + H_2O.$$

The salt $Na_2HAsO_4,12H_2O$ is largely used in calico-printing. Arsenic acid is an oxidising agent ; 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, when arsenates are reduced to arsenites, phosphates are unaltered. $As_2O_5 + 2SO_2 = As_2O_3 + 2SO_3$. The excess of sulphur dioxide is removed from the solution by boiling, and a current of hydrogen sulphide 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 *light 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, which occur native as the yellow and red minerals *orpiment* and *realgar*, respectively, 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 by distilling iron pyrites with arsenical pyrites : $2FeS_2 + 2FeAsS = As_2S_2 + 4FeS$.

The trisulphide is easily prepared by passing hydrogen sulphide through a solution of arsenic trioxide in dilute hydrochloric acid :

$$2AsCl_3 + 3H_2S = As_2S_3 + 6HCl.$$

If hydrogen sulphide is passed into a solution of arsenious oxide in distilled water, no precipitate is formed but a yellow colloidal solution of arsenic trisulphide is produced. Addition of dilute hydrochloric acid or salts at once coagulates it 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. The amounts of electrolyte in millimols required to coagulate an arsenious sulphide sol. are (Picton and Linder, 1895) Na Cl′ 51·0, Ca Cl′$_2$ 0·65 ; Al ˙˙Cl′$_3$ 0·09. The great effect of the increasing charge on the cation is clear.

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, under the name of "Rusma," for removing superfluous hair In both cases the active agent is probably calcium hydrosulphide, $Ca(SH)_2$, which dissolves hair. A mixture of orpiment (the *auripigmentum* of the Romans) with the trioxide, obtained by subliming the latter with sulphur, is the pigment *King's yellow*

Both sulphides of arsenic burn when heated in air, forming sulphur dioxide and volatile arsenic trioxide. They are oxidised by nitric acid but are insoluble in hot concentrated hydrochloric acid (Sb_2S_3 is soluble).

Arsenic pentasulphide, As_2S_5, is said to be formed when hydrogen sulphide is passed rapidly into a warm solution of arsenic acid containing 10–12 per cent of free hydrochloric acid : $As_2O_5 + 5H_2S = As_2S_5 + 5H_2O$. The first product is the unstable thioarsenic acid, H_3AsO_3S If the reaction takes place slowly and in the cold, a white precipitate of sulphur is first formed and the arsenic acid is reduced to arsenious acid. On further passing the gas, the arsenious acid is precipitated as arsenious sulphide .

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S ;$$
$$2H_3AsO_3 + 3H_2S = As_2S_3 + 3H_2O.$$

The reaction is quicker in hot solutions. In qualitative analysis, solutions of arsenates are first reduced with sulphurous acid before treating with hydrogen sulphide.

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** :

$$As_2S_3 + 6KOH = K_3AsO_3 + K_3AsS_3 + 3H_2O.$$

If an acid is added, the whole of the arsenic is precipitated as sulphide :

$$K_3AsO_3 + K_3AsS_3 + 6HCl = 6KCl + 3H_2O + As_2S_3.$$

If arsenic trisulphide is dissolved in an alkali-sulphide, a thio-arsenite alone is formed :

$$3K_2S + As_2S_3 = 2K_3AsS_3.$$

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.

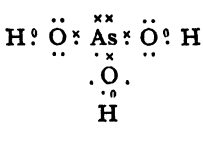
Thioarsenites are derived from hypothetical thioarsenious acids : H_3AsS_3 (*ortho*) ; $H_4As_2S_5$ (*pyro*) ; $HAsS_2$ (*meta*), but they (like the arsenites) have not been much investigated Berzelius, who first prepared the salts, recognised that sulphur in them takes the place of oxygen as the " acidifying principle."

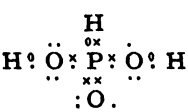
When arsenic trisulphide is boiled with sodium carbonate solution, carbon dioxide is evolved, arsenic disulphide (As_2S_2) is precipitated, and a solution of a thioarsenite is formed On fusing the trisulphide with sodium carbonate, arsenic sublimes and the residue contains an arsen*ate* and thioarsen*ate*. Arsenic also sublimes when the sulphide is fused with sodium carbonate and potassium cyanide . it is said that none then remains in the residue.

If arsenious sulphide is dissolved in an alkali polysulphide, *e.g.*, yellow ammonium sulphide, $(NH_4)_2S_2$, or a thioarsenite is digested with sulphur, a solution of a **thioarsenate** is obtained : $K_3AsS_3 + S = K_3AsS_4$. 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.*, $Na_3AsO_3S,12H_2O$; K_3AsOS_3 ; $Na_2HAsO_3S,8H_2O$, $Na_3AsO_2S_2,11H_2O$. These are 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.

Although the electronic formulae of arsenic compounds may be generally regarded as analogous to those of phosphorus, arsenious acid, H_3AsO_3, is a tribasic acid and its formula is different from that of phosphorous acid (p. 631), which is dibasic :





CHAPTER XXXIV

CARBON AND THE HYDROCARBONS

Carbon and its compounds.—The element carbon is found in Nature both in the free state and in combination. The element 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 the presence of carbon in the sun and some stars. Mixtures of hydrocarbons compose mineral oil or *petroleum*. Coal contains complex hydrocarbons, but oxygen and nitrogen are also present. **Carbon dioxide,** CO_2, occurs uncombined in the atmosphere and combined as **carbonates,** especially **calcium carbonate,** $CaCO_3$ (*chalk*, *limestone*, and *marble*), **magnesium carbonate,** $MgCO_3$ (*magnesite*), and 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 **organic compounds** of carbon with hydrogen and oxygen and sometimes nitrogen, sulphur, and phosphorus. 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.

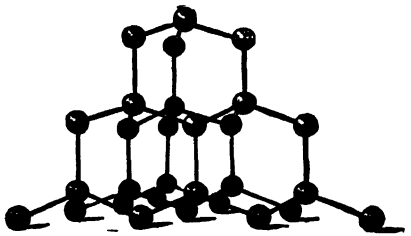


FIG. 294.—The linking of carbon atoms in diamond.

Carbon forms such a large number of compounds owing to the facility with which its atoms, unlike those of most other elements, combine to form chains (**aliphatic,** or **fatty, compounds**), or rings (**cyclic,** or **aromatic, compounds**).

By means of the X-rays the arrangement of the atoms of carbon in diamond and graphite has been elucidated; the lattices are described on p. 431, but the linkings of the atoms are redrawn in Figs. 294 and 295. It will be seen that each atom is joined to another by four valencies, but whereas these are equally distributed in diamond, in graphite one of

the valencies joins an atom with another in a plane at a greater distance and this binding is much less firm than that in diamond. The hexagonal arrangement in graphite and the tetrahedral arrangement in diamond are clearly seen.

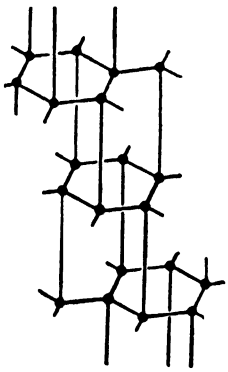


FIG 295.—The linking of carbon atoms in graphite

Allotropic forms of carbon.—Carbon is a striking example 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 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 diamond would appear improbable; its analogy with graphite or black-lead would seem clearer, by reason of the colour, yet it is curious that the composition of diamond was elucidated (1772) 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. The amounts of heat liberated in the three cases, however, are different: for 12 gm. of carbon they are: graphite, 94·26 k. cal.; diamond, 94·43 k. cal.; charcoal, 96·72 k. cal. These differences are supposed to be due to different modes of linkage of the carbon atoms in the substances. Since the binding is very firm, the hardness of diamond and the high melting point are explained.

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, British Guiana, New South Wales, Arkansas and particularly in British South Africa. Most diamonds are small but the Cullinan diamond, discovered at Kimberley in 1905, weighed about $1\frac{1}{8}$ lb., or 3032 carats (1 *carat* = 0·2054 gm. The International carat = 0·200 gm.) This is the largest yet discovered, and was cut into two brilliants of 516·5 and 309 carats. The South African mines supply over 96 per cent. of the diamonds of the world.

Large colourless diamonds are the Pitt diamond (136·25 carats), and the Koh-i-noor, originally 186 carats but reduced to 106 by recutting. The Hope diamond, 44·5 carats, is a fine blue stone. The cause of the colour of diamonds is not clear: exposure to cathode rays may deepen the colour, which is lost on heating to 300°–400°, except in the case of yellow, which is very stable.

Black or dark-coloured (green, brown, red or grey) diamonds, known as *carbonado* and *bort* (or *boart*) are of no value as gems but are very hard, and are used for rock-drills, for lathe tools for setting abrasive wheels, for dies for wire-drawing (*e.g.*, tungsten filaments for lamps) and when crushed for cutting and polishing clear diamonds. The latter are pressed against a revolving metal disc, covered with diamond powder and oil. Only about 42 per cent. of the original weight remains after cutting.

Boart may mean any impure diamond or even fragments of gem diamonds *Carbonado* is usually understood to mean a massive form, granular and without cleavage, or an impure aggregate of small crystals. According to Roth (1925) the heats of combustion of colourless diamond and *carbonado* are 7·873 k. cal. and 7·884 k. cal. per gm. respectively.

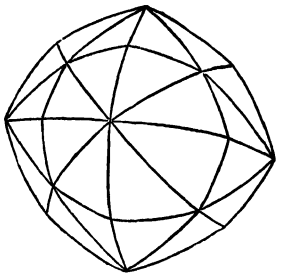


FIG. 296.—Diamond crystal

The diamond crystallises in the regular (or cubic) system; forms related to the cube or the octahedron, sometimes with curved faces, predominate (Fig. 296). 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. 297).

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, eclogite, 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.

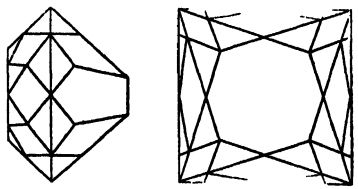


FIG. 297.—Diamond cut as "brilliant."

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. 3. Calcite. 5. Apatite. 7. Quartz. 9. Corundum.
2. Gypsum. 4. Fluorite. 6. Orthoclase 8. Topaz. 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 density of 3·520, a high refractive index (2·417 for the D-line), and a high dispersive power, exhibiting a play of colours in white light. It is transparent to X-rays, whilst all imitations are opaque. The diamond is coloured green by α-rays from radium. Many diamonds phosphoresce in cathode rays or ultra-violet light. 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.

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 blackened. Doelter does not consider that any transformation to graphite occurs; Arnberg states that it is transformed into graphite, which according to Kohlschutter is the stable form at high temperatures and ordinary pressure, and is produced from diamond and amorphous carbon alike. If heated at 900° in air or 700° in oxygen, the diamond burns, leaving only a trace of ash (0·05–0·2 per cent., chiefly silica and oxide of iron); boart may leave as much as 4·5 per cent. of ash. Diamonds are attacked by fused sodium carbonate. The ignition temperature of boart is higher than that of clear diamond.

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. Allen and Pepys in 1807 burnt diamond in oxygen and showed that it gave the same weight of carbon dioxide as charcoal Davy in 1814, 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 Smithson Tennant (1797) burnt diamonds by strongly heating them in a gold tube with fused nitre (first used for this purpose by Guyton de Morveau in 1785): he found

that as much carbon dioxide was formed as Lavoisier had obtained in 1772 from an equal weight of charcoal.

EXPT. 1.—The combustion of the diamond in oxygen may be exhibited by heating a splinter of *carbonado* by an electric current in a spiral of fine platinum wire supported by copper leads inside a jar of oxygen (Fig. 298). A little lime-water is shaken up with the gas afterwards.

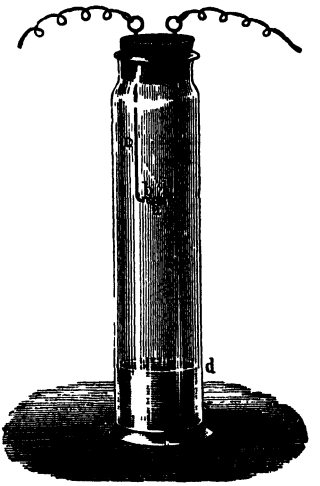


FIG. 298.—Combustion of the diamond in oxygen.

After many unsuccessful attempts to prepare diamonds artificially, the problem was to some extent solved by Moissan in 1893. He heated charcoal at a very high temperature with iron in the electric furnace, in which an electric arc is struck between carbon rods inside blocks of limestone (Fig. 299). Fused iron dissolves carbon; 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° by plunging the crucible taken from the electric furnace into water. 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. Moissan at first considered that the important condition was the enormous pressure developed by the solidification of the molten cast-iron inside the rigid outer skin which was first formed, but he afterwards gave up this idea and thought rapid cooling was the essential condition. Moissan's experiment has been successfully repeated by Crookes, La Rosa, and Ruff (1917). The largest artificial diamond obtained measured 0·7 mm.

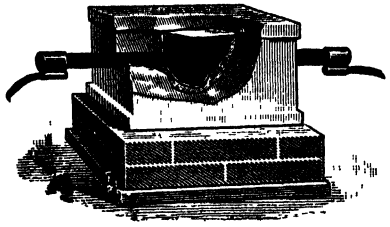


FIG 299 —Moissan's electric furnace

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 *molybdoena* or *black-lead*, since both were soft grey 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; the name is due to Werner), 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 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 1855, after which it was recognised that graphite is merely an allotropic form of carbon.

Graphite is found in Borrowdale in Cumberland (the mines are worked out), Siberia, Ceylon and Bohemia, and 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 The Ceylon graphite is purest and is the best for many purposes, but the Siberian and Bohemian varieties are most used for making pencils.

Graphite is produced artificially by the Acheson process (1896) at Niagara. 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 on a brick furnace and covered with sand (Fig. 300). 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).

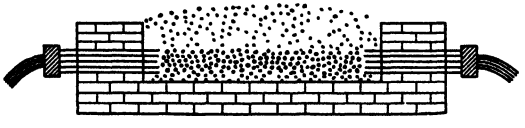


FIG. 300.—Production of graphite in the electric furnace.

The product is very pure and soft, and free from grit. It is used for electrodes, brushes, carbons for dry batteries, and as a lubricant, but not for pencils. 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 plates belonging to the hexagonal (or trigonal) 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 when pure a specific gravity of 2·25, and is a good conductor of heat and electricity · on account of the latter property it is used in the cores of arc-carbons, as anodes for electrolytic cells and for covering plaster moulds on which copper is deposited by electrodeposition. 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. Conrad Gesner in 1565 describes a lead pencil made with *stimmi Anglicum*, *i.e.*, Borrowdale graphite

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. It burns brilliantly in fused nitre at a high temperature. Graphite is not attacked by fused sodium sulphate, which dissolves coke and retort carbon, but it gives carbon monoxide with fused sodium carbonate. When moistened with concentrated nitric acid and then heated some varieties of graphite (Borrowdale and Austrian) do not swell up: others (Ceylon and American) do. The two forms are sometimes called *graphite* and *graphitite*, respectively. 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 micro-crystalline or amorphous in appearance, and has the formula $C_{11}H_4O_5$. According to Hulett and Nelson

(1920), it is "a colloidal oxide of carbon" C_3O, or $C_{11}O_4$. X-ray examination, however, shows that it is crystalline. On heating at 200° it swells up and leaves a fine black powder of **pyrographitic oxide**, $C_{22}H_2O_4$ (?) and finally graphite. When treated with hydriodic acid, graphitic acid takes up hydrogen, forming **hydrographitic acid**, which does not yield pyrographitic oxide on heating.

One gm of pure powdered Ceylon graphite is added to a cooled mixture of 40 c.c. of conc H_2SO_4 and 20 c.c. of 60 per cent. HNO_3. To the mixture are added, in small portions over a period of 1½ hours, 20 gm. of $KClO_3$, with shaking. The mixture is allowed to stand 16 hours and then poured into 1 litre of distilled water. The graphitic acid is washed by decantation till free from acid, filtered (it is difficult to filter) and dried in a desiccator over P_2O_5, when it forms a mass like varnish (U. Hofmann, 1928).

According to Brodie, and Berthelot, pure graphitic acid is crystalline and bright yellow when moist. The crude greenish product is purified by treatment with acidified permanganate and becomes yellow. It is brown when dry.

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.

According to Roth (1925) there are two varieties of graphite, **α-graphite** and **β-graphite**, but these are distinguished only by their different heats of combustion, 7 832 k. cal. and 7·856 k. cal. per gm., respectively.

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 all contain microcrystalline material, 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 re-crystallised cane-sugar in a large covered crucible until gases cease to be evolved; the resulting charcoal is heated at 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 in oxygen:

	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 thermal 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° black 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 good charcoal is about 93; it contains about 1·5 per cent. of oxygen, 2·5 per cent. of hydrogen and 3 per cent. of ash. 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,

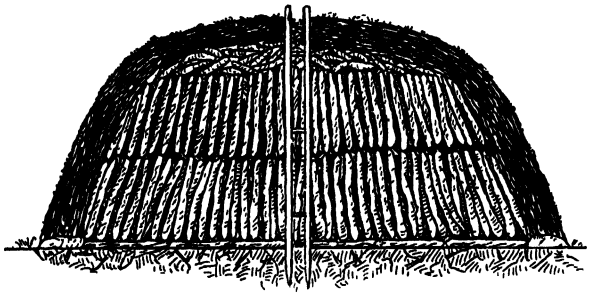


FIG. 301 —Charcoal "Meiler."

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. 301). 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.

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 by weight of dry wood are: 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 1·3–1·9, 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 Caesar, were found nearly two thousand years later, and still sound at heart.

In virtue of its great porosity, charcoal readily absorbs (or adsorbs) gases (Scheele, and Fontana, 1777).

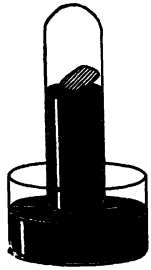


FIG 302.—Absorption of ammonia gas by charcoal.

EXPT. 2.—If a piece of recently ignited wood-charcoal is passed into a tube of ammonia gas standing over mercury (Fig. 302), the gas is rapidly absorbed, the charcoal takes up about 90 times its volume of ammonia gas.

A very active form of charcoal is prepared by heating the shell of the coconut; 1 volume of such charcoal, quenched under mercury, adsorbs 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
Nitrous oxide	86·3	Carbon monoxide	21·2
Ethylene	74·7	Oxygen	17·9
Nitric oxide	70·5	Nitrogen	15

The preferential adsorption of ethylene by charcoal is applied in its extraction from coal gas Vapours of volatile liquids are adsorbed even more readily than gases the volumes of ammonia, carbon dioxide, steam and alcohol vapour adsorbed at 126·5° are 21·9, 16·6, 43·8, and 110 8 respectively. Generally speaking, the adsorption increases the nearer the gas or vapour is to its point of liquefaction at the temperature of the experiment. McBain found 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 At low temperatures the adsorbed amount increases rapidly (Dewar, 1904).

Gas	He	H_2	A	N_2	O_2	
0°	2	4	12	15	18	volumes at S T P
−185°	15	35	175	155	230	

EXPT. 3 —The condensed layer of gas held by the charcoal is very reactive (Stenhouse, 1855) Lower a crucible containing powdered, recently ignited, charcoal in a jar of hydrogen sulphide After it has become saturated with the gas, transfer it to a jar of oxygen Ignition occurs

Chlorine adsorbed 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, respectively.

Charcoal also takes up many substances from solutions, *e.g.*, metallic salts, organic substances such as alkaloids (*e.g.*, quinine), and colouring matters (Lowitz, 1790). It removes fusel oil (amyl alcohol) from crude spirit.

EXPT. 4.—Boil solutions of litmus and indigo with finely-powdered animal charcoal, and filter. The filtrates are colourless

A very active form of charcoal, " active charcoal," used in gas-masks, is obtained by heating charcoal (*e g.*, of birch wood) at 900° in a very limited supply of air or in steam, when the material obstructing the pores is removed. It is also obtained by carbonising wood which has been treated with salts such as zinc chloride or magnesium chloride, which are removed from the charcoal by washing with water or acids It adsorbs very much larger volumes of gas than ordinary charcoal. Active charcoal is also used, as well as animal charcoal and blood charcoal, in decolorising sugar syrup (Derosne, 1812), or for removing fusel oil from crude spirit.

The decolorising charcoal is revivified by boiling it with caustic soda solution and washing. Bone black is revivified by heating to redness in closed retorts.

Animal charcoal.—This material, also known as *bone-black*, is prepared by the destructive distillation of degreased 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 together with calcium carbonate, etc If the phosphate and other salts are dissolved out by hydrochloric acid, the charcoal remains as **ivory black.**

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 by burning oil, tar, creosote oil, resin, 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 from steatite burners under a cooled rotating metal disc or rollers, or (usually) iron bands (" channels "), the whole being in an iron shed The *gas black* (called *carbon black* in America) is removed by scrapers. A variety of carbon black is prepared at Shawinigan by the explosion of acetylene (from refuse carbide) and air under pressures of 50–100 lb. per sq. in., or by burning the gas from burners. Most of the carbon black is used as a filler in rubber tyres ; some is used as a pigment.

Lampblack contains oily impurities which may be removed by ignition in chlorine, as in the case of sugar charcoal; it is then a pure form of carbon. The density is 1·78.

Coal.—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 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. The constituents have different adsorptive capacities for pyridine vapour.

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 but 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.

The next stage of the process leads to the types of **bituminous coal**, *i.e.*, common coal. These are complex: distinct evidences of fossilised vegetables are still present. Bituminous coals burn with a bright smoky flame, and are divided into *caking* and *non-caking* according as they do or do not soften and fuse together on burning or coking **Cannel coal** is a compact, dull grey or black, non-lustrous variety, 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. **Jet**, found at Whitby, etc., is a hard lustrous variety of cannel coal.

The last 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 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.

The following table shows the change in composition which occurs during the conversion of woody matter (lignin) into coal, with the corresponding increase in calorific value.

	Carbon.	Hydrogen.	Oxygen	Calorific Value B Th U per lb
Wood	50·0	6·0	44 0	7,400
Peat	60·0	5 9	34·1	9,900
Lignite	67 0	5 2	27·8	11,700
Bituminous coal	88·4	5 6	6 0	14,950
Welsh steam coal	92 5	4·7	2·7	15,720
Anthracite	94 1	3·4	2 5	15,720
Pure charcoal	100·0	—	—	14,544
Petroleum	85 5	14·2	0 3	19,800
Coal gas	—	—	—	19,220
Hydrogen	—	100 0	—	62,100
Methylated spirit	52 2	13 0	34 8	11,160

(The values for wood, peat, etc., refer to materials free from moisture: the actual materials contain water and the calorific values are smaller than those given The values for pure charcoal, coal gas, hydrogen, methylated spirit, and petroleum are given for comparison.)

In the **Bergius process** powdered coal is partly converted into a hydrocarbon oil by heating it with hydrogen gas and coal oil under great pressure

The **calorific value** 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. It is determined by burning a weighed amount of the fuel in compressed oxygen in a strong metal **bomb calorimeter** (Fig. 303). The fuel is ignited by a known weight of iron wire heated by an electric current and supported over a platinum spoon containing the fuel The bomb is immersed in water in a calorimeter. The heat of combustion of the iron wire is subtracted from the total heat evolved.

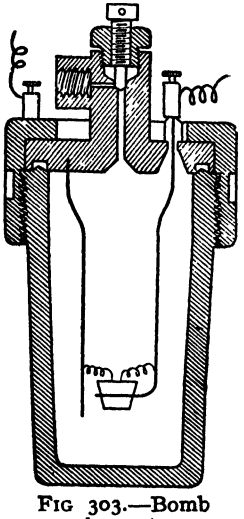


FIG 303.—Bomb calorimeter

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 strontium and barium are produced by heating the oxides with carbon in the electric furnace: $MO + 3C = MC_2 + CO$. Beryllium combines directly with carbon, forming Be_2C. 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**: $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. Beryllium and aluminium carbides give **methane**: $Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$. The carbides of some 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.

Hydrocarbons.

Methane.—Methane, CH_4, is formed by the bacterial decay of vegetation (cellulose) at the bottom of marshy pools, and the *marsh gas* liberated in bubbles when the mud is disturbed with a stick consists mainly of methane and carbon dioxide. It also occurs occluded in coal and escapes when the pressure is relieved, forming *fire-damp*, 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 the gas from some kinds of rock salt is rich in methane.

Methane is formed by the direct union of carbon and hydrogen at high temperatures: $C + 2H_2 \rightleftharpoons CH_4$. 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 is passed over reduced nickel at 250° to 400°: $CO + 3H_2 = CH_4 + H_2O$

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. 304):

$$CH_3{\cdot}COONa + NaOH = Na_2CO_3 + CH_4.$$

It is collected over water. Prepared in this way it is not very pure and 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.

Pure methane is prepared by the action of water on zinc methyl:

$$Zn(CH_3)_2 + 2H_2O = Zn(OH)_2 + 2CH_4.$$

Pure methane is best prepared by the action of zinc-copper couple, or amalgamated aluminium, on methyl iodide and methyl alcohol:

$$CH_3I + CH_3OH + Zn = ZnI(OCH_3) + CH_4;$$
$$2Al + 3CH_3I + 3CH_3OH = Al(OCH_3)_3 + AlI_3 + 3CH_4.$$

The zinc-copper couple is prepared by shaking dry zinc dust with one-tenth of its weight of dry copper oxide in a flask. The latter is then

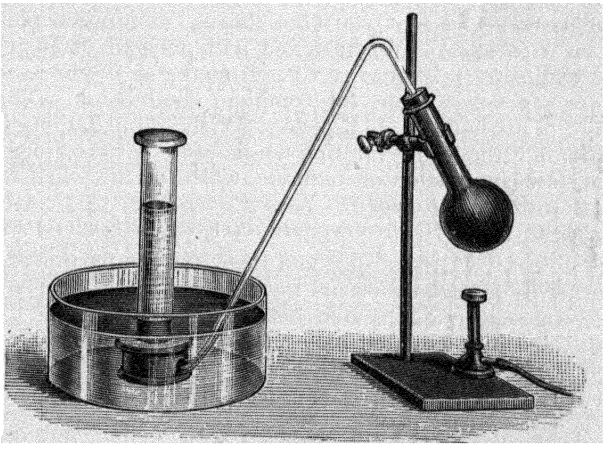


FIG. 304.—Preparation of methane.

fitted with a dropping funnel and a vertical tube containing granulated zinc which has been immersed in copper sulphate solution. A mixture of equal volumes of methyl iodide and methyl alcohol is dropped slowly on the couple, the flask being gently warmed if necessary. The methane passes through the coppered zinc, which frees it from methyl iodide vapour, and is then collected over water. Amalgamated aluminium is more active. It is made by immersing small pieces of sheet aluminium in mercuric chloride solution and washing in dry methyl alcohol. It is packed into a U-tube cooled in ice and is covered with methyl iodide. The mixture of methyl iodide and methyl alcohol is dropped on from a tap funnel fitted to one side of the U-tube and the gas evolved passes out through a delivery tube.

A fairly 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 or palladium asbestos at 100°. The excess of oxygen is then removed by pyrogallol.

Properties of methane.—Pure methane is a colourless odourless gas which is not poisonous, b. pt. −161·4°, m. pt. −185·8°. The critical temperature and pressure are −82·85° and 45·6 atm. The density of methane is 0·7168 gm./lit.; the theoretical value is 0·7154; hence the gas is slightly more compressible than an ideal gas. It is sparingly soluble in water: 100 vols of water dissolve 5·56 vols. at 0°, and 3·3 vols at 20°; it 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, slightly luminous flame: $CH_4 + 2O_2 = CO_2 + 2H_2O$; its ignition point in air is high, viz 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 5·6 by volume: the lowest ignition temperature is stated to be 500°

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 **formaldehyde**, H·COH, are formed: $CH_4 + O_2 = H{\cdot}COH + H_2O$.

According to H E Armstrong, and 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, in turn, may undergo oxidation or thermal decomposition

$$CH_4 \rightarrow \underset{\text{methyl alcohol}}{CH_3OH} \rightarrow \underset{\text{unknown in free state}}{CH_2(OH)_2} \rightarrow \underset{\text{formaldehyde}}{H{\cdot}CHO} \rightarrow \underbrace{H\,COOH}_{\text{formic acid}} \rightarrow \underbrace{HO{\cdot}CO{\cdot}OH}_{\text{carbonic acid}}$$

$$\overbrace{CO + H_2O} \qquad \overbrace{CO_2 + H_2O}$$

At 360° and 100 atm. pressure, up to 17 per cent. of methane may rapidly be oxidised to methyl alcohol, with only 0 6 per cent. to formaldehyde and no trace of peroxide. Under ordinary conditions formaldehyde is the first product detected.

According to another theory, unstable peroxides are first formed and then decompose, the products being further oxidised by excess of oxygen into oxides of carbon and water

Dalton (1805) found that when methane is mixed with its own volume of oxygen, "the least that can be used with effect," and fired, the mixture explodes without appreciable change in volume, with formation of carbon monoxide and hydrogen: $CH_4 + O_2 = CO + H_2 + H_2O$. "Each atom of gas requires only 2 atoms of oxygen; the one joins to one of hydrogen and forms water [HO, according to Dalton]; the other joins to the carbone to form carbonic oxide, and at the

same moment the remaining atom of hydrogen springs off." On adding a further volume of oxygen, the gas may again be fired :

$$CO + H_2 + O_2 = CO_2 + H_2O.$$

A mixture of 1 vol. of methane with 2 vols. of chlorine, ignited by a taper, 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 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.

Mixtures of all the substances are usually produced. Since methane can react only by substitution or decomposition, not by addition, it is called a **saturated hydrocarbon.**

Ethylene.—By the interaction of hydrogen and carbon at high temperatures, besides methane, traces of ethylene 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 formed from alcohol vapour in contact with thorium dioxide or alumina heated at 340°–350° : $C_2H_5OH = H_2O + C_2H_4$.

Ethylene is prepared by dehydrating ethyl alcohol by means of zinc chloride, boron trioxide, phosphorus pentoxide, concentrated sulphuric acid, or syrupy phosphoric acid : $C_2H_5OH = C_2H_4 + H_2O$. With sulphuric acid, ethylsulphuric acid, $C_2H_5HSO_4$, is first formed and then decomposed : (1) $C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$. (2) $C_2H_5HSO_4 = H_2SO_4 + C_2H_4$. This method of preparation appears to have been discovered by Becher (1669).

EXPT. 5.—30 c c of alcohol and 80 c c of concentrated sulphuric acid are heated in a 2–3 litre flask at 160°–170°, and a mixture of equal volumes of alcohol and 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. 205).

EXPT. 6.—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, which may be collected over saturated sodium sulphate solution.

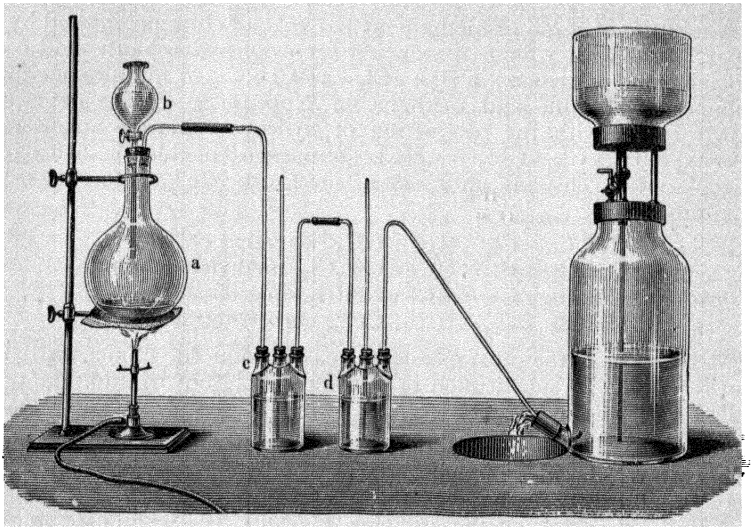


FIG. 305.—Preparation of ethylene.

Properties of ethylene.—Ethylene is a colourless gas with a peculiar sweet smell and has been used as an anaesthetic and for " ripening " fruit. It is slightly soluble in water, and very soluble in alcohol. B. pt. $-103{\cdot}7°$, m. pt. $-169{\cdot}5°$; critical temperature $9{\cdot}5°$, critical pressure 50·65 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 :

$$H_2C{:}CH_2 \rightarrow 2CH\dot{:} + H_2 \rightarrow \begin{cases} (a)\ C_2H_2 + H_2. \\ (b)\ 2C + H_2 + H_2. \\ (c)\ C_2H_2 + 3H_2 = 2CH_4. \end{cases}$$

The radical $CH\dot{:}$ is supposed to have a transient existence : it may undergo polymerisation, with formation of complex ring compounds (*cf.* p. 670).

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: $2CO + 2H_2 + 2O_2 = 2CO_2 + 2H_2O$ (Dalton, 1810).

The combustion of ethylene is represented in Bone's scheme as follows

$$H_2C{:}CH_2 \rightarrow \overbrace{CH_2\ CH(OH)}^{\text{vinyl alcohol}} \rightarrow \overbrace{(HO)\,CH\ CH(OH)}^{\text{hypothetical}}$$

$$\overbrace{CH_3\,CHO}^{\text{acetaldehyde}} \qquad \overbrace{2H\,COH}^{\text{formaldehyde}} \rightarrow \overbrace{H\,COOH}^{\text{formic acid}} \rightarrow \overbrace{HO\,CO\,OH}^{\text{carbonic acid}}$$

$$\overbrace{H_2O + CO} \qquad \overbrace{H_2O + CO_2}$$

The production of hydrogen in the incomplete explosive combustion of hydrocarbons is considered as due to the secondary thermal decomposition of the formaldehyde $HCOH = H_2 + CO$.

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:

$$H_2C{\cdot}CH_2 + Cl_2 = CH_2Cl{\cdot}CH_2Cl.$$

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, Bondt, Lauwerenburgh, and Paets van Troostwijk, in 1795. 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 combines with iodine, hydrobromic acid, and hydriodic acid at 100°, but not with hydrochloric acid: $CH_2.CH_2 + HBr = CH_3\,CH_2Br$. 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 chloro hydrin**: $CH_2{:}CH_2 + HOCl = CH_2OH{\cdot}CH_2Cl$. Cold dilute potassium permanganate solution is decolorised by ethylene, hydrated manganese dioxide is deposited, and the ethylene is oxidised to **glycol**:

$$CH_2.CH_2 + H_2O + O = CH_2OH \cdot CH_2OH.$$

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.—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, and by direct synthesis from its elements when an electric arc burns between carbon poles in an atmosphere of hydrogen (Fig. 306): $2C + H_2 \rightleftharpoons C_2H_2$. Small quantities of methane and ethane are also formed, apparently by independent reactions.

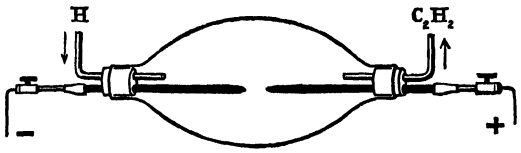


FIG 306.—Berthelot's synthesis of acetylene

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 acetylene, although 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. 7.—The presence of acetylene in the gas issuing from the burner is detected by holding over it a globe wetted inside with an ammoniacal solution of cuprous chloride. The dark blue liquid rapidly becomes covered with a red film, owing to the precipitation of **cuprous acetylide,** Cu_2C_2, an explosive substance.

Acetylene is actually prepared by the action of water on calcium carbide: $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2\uparrow$.

EXPT. 8.—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 307). 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, which are removed by passing through a solution of bleaching powder.

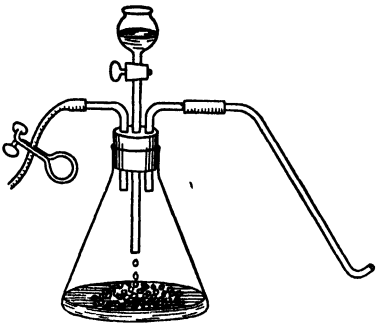


FIG. 307.—Preparation of acetylene.

Acetylene generators used for the preparation of the gas act either on the principle of the Kipp's apparatus, or else a regulated stream of water is allowed to drop on the carbide.

Pure acetylene is obtained by decomposing cuprous acetylide with potassium cyanide solution, or 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

$$CH_2Br{\cdot}CH_2Br = CH \quad CH + 2HBr.$$

The compound C_2H_3Br is formed in an intermediate stage.

Properties of acetylene.—Acetylene is a colourless gas with an ethereal smell when pure, but ordinarily has an unpleasant odour. When strongly cooled it forms a white solid, subliming at $-82{\cdot}4°$. Under 1·25 atm. pressure the solid melts at $-81°$ to a colourless liquid. The critical temperature is $35{\cdot}5°$; the critical pressure 61·65 atm. The gas dissolves in its own volume of water, and is very soluble in alcohol. Acetylene ignites at 406°–440° in air, burning with a very smoky, luminous flame, but if 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 5·6 per cent. in air. The danger of explosion with acetylene is, therefore, much greater than with coal gas.

Acetylene forms with the haemoglobin 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: $2C + H_2 = C_2H_2 - 47{\cdot}8$ k. cal., is unstable, and readily explodes under moderate pressure. It 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 steel bottles. 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 explodes violently with the gas, but by passing the two gases alternately into sulphur chloride containing a little reduced iron, combination occurs, forming the dichloride, CHCl CHCl, and the tetrachloride, $CHCl_2$ $CHCl_2$ 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 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 CHO, is continuously formed and distils off The first reaction is the formation of a mercury compound which is decomposed by the acid From acetaldehyde, by reduction with hydrogen, alcohol, CH_3 CH_2 OH, can be obtained , on oxidation, aldehyde yields acetic acid, $CH_3 \cdot COOH$.

The combustion of acetylene is represented by Bone according to the scheme .

$$HC \cdot CH \rightarrow \overbrace{(HC\ O)_2}^{\text{glyoxal}}$$

$$\overbrace{CO + H\ COH}^{\text{formaldehyde}} \rightarrow \overbrace{H\ COOH}^{\text{formic acid}} \rightarrow \overbrace{HO \cdot CO\ OH}^{\text{carbonic acid}}$$

$$\overbrace{H_2O + CO} \qquad \overbrace{H_2O + CO_2}$$

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 radical CH :, which also decomposes into carbon and hydrogen, the latter combining with the CH : to form methane, CH_4

The composition of gaseous hydrocarbons.—When a measured volume of a gaseous hydrocarbon is mixed in a eudiometer with a measured excess of oxygen, and the mixture exploded by a spark, water and carbon dioxide are formed :

$$C_mH_n + (m + \tfrac{1}{4}n)O_2 = mCO_2 + \tfrac{1}{2}nH_2O.$$

The water condenses to liquid on cooling and the carbon dioxide may be absorbed by a solution of caustic potash, and hence its volume found. The residual gas is the excess of oxygen used.

Since the volume of carbon dioxide is equal to the volume of oxygen used in burning the carbon, say m c.c., then if x c.c of oxygen were originally taken and z c.c remain unabsorbed after the experiment, it follows that the volume of oxygen used in the combustion of the hydrogen is $y = x - (m + z) = \frac{1}{2}n$ c.c. This volume of oxygen would correspond with a volume $2y$ or $\frac{1}{2}n$ of hydrogen existing in the free gaseous state. Each volume of carbon dioxide corresponds with one atom of carbon and each volume of hydrogen with two atoms of hydrogen Thence the composition of the hydrocarbon is easily calculated

The results of such experiments are most conveniently exhibited in a table. To avoid decimals, larger volumes of gas are specified than would conveniently be used.

Gas	Vol taken	Vol of oxygen added	Vol after explosion	Contraction with potash $=$ vol CO_2	Residual oxygen	Vol of O_2 combg with H_2	Vol of hydrogen
Methane -	30 c.c	66 c c	36 c c	30 c c	6 c.c	30 c c	60 c c.
Ethylene -	30 ,,	95 ,,	65 ,,	60 ,,	5 ,,	30 ,,	60 ,,
Acetylene -	10 ,,	30 ,,	25 ,,	20 ,,	5 ,,	5 ,,	10 ,,

The table shows that 1 vol of methane gives 1 vol of carbon dioxide and contains an amount of hydrogen equivalent to 2 vols. in the free state Thus, 1 molecule of methane contains 1 atom of carbon and 2 molecules or 4 atoms of hydrogen, and its formula is CH_4 This is confirmed by the relative density. Similar reasoning shows that the formulae of ethylene and acetylene are C_2H_4 and C_2H_2 respectively The explosion of acetylene with oxygen in a eudiometer is dangerous and special precautions must be taken

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 Murdock 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 Salford factories in 1805, the first public gas-works being erected there, and about the same time gas lighting was used on a very small scale in London The capital was partly 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 "carbonised" in fireclay retorts (Fig. 308) heated by producer gas formed by passing air and steam through incandescent coke beneath each retort. The gas evolved from the coal passes by way of vertical ascension pipes to a long horizontal hydraulic main, which serves as 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, a series of vertical iron cooling pipes. Ammoniacal liquor is deposited with the tar, and the two collect in the tar-well. The gas next passes to a special tar separator and to the washer, an iron tower packed with coke, down which water passes, which removes the rest of the ammonia.

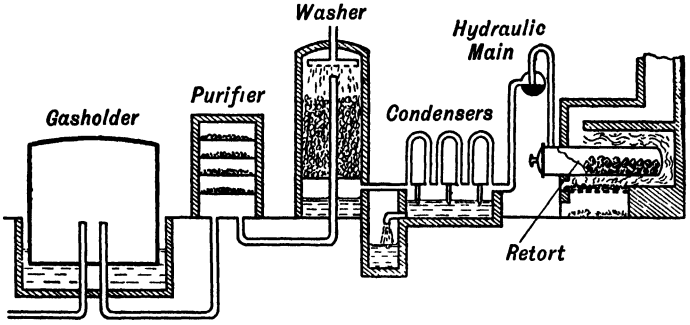


FIG 308 —Coal-gas manufacture.

The scrubbed gas 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. 100 cubic feet of crude gas usually contain 400 grains of sulphur as H_2S and 40 grains as CS_2. The CO_2 and H_2S are removed by purifiers, 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 : $Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$. The oxide is " revived " by exposure to air, when sulphur is separated and hydrated ferric oxide regenerated : $2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S$. 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 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 passes to the gas-holder, a counterpoised iron bell sealed below by water, or an iron tower with a piston sealed by flowing tar. 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 a washer containing ferrous sulphate and alkali, when ferrocyanide is produced, or 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 value of good coal gas is about 19,000 B.Th.U. per lb. or 600 B.Th U. per cu. ft. Modern coal gas is usually mixed with water gas, produced by blowing steam over the red-hot coke in the retorts $C + H_2O \rightleftharpoons CO + H_2$ In this way the percentage of carbon monoxide is increased, and that of methane diminished

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 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.

According to Hofmann and Röchling it is a mixture of graphite with a very hard variety of carbon, which they call **lustrous carbon,** silvery in appearance, sp. gr. 2·07, which is a moderately good conductor of electricity and is deposited on a glazed porcelain surface at 800°–1000°, from gas containing methane, in the form of a brilliant layer It is chemically very indifferent, resisting nitric acid and even fused sodium sulphate.

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.

EXPT. 9.—The effect of such hydrocarbons on the luminosity of flames may be illustrated by fitting a brass jet to each arm of a Y-tube, in one arm of which is a piece of cotton-wool soaked in benzene (Fig. 309), attaching the tube to a hydrogen apparatus, and lighting the two jets. The hydrogen saturated with benzene vapour burns with a luminous flame

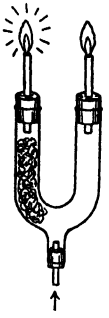


FIG. 309.—Luminosity imparted to hydrogen flame by benzene vapour

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 quenched with water. It is known as gas coke, and used as fuel. It is greyish-black, porous, and brittle, and contains all the ash of the coal, about half 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.

The yields from 1 ton of Newcastle coal in gas-making, are: 12,500 cu. ft. of gas; 1 gallon of light oil scrubbed from the gas, 110 lb. of tar, yielding 77 lb. of pitch, 7 lb. of ammonia, and 65–70 per cent. of the weight of the coal as coke.

A hard variety of coke for metallurgical purposes (*e.g.*, blast furnaces) is prepared by carbonising coal in **coke-ovens**. The old

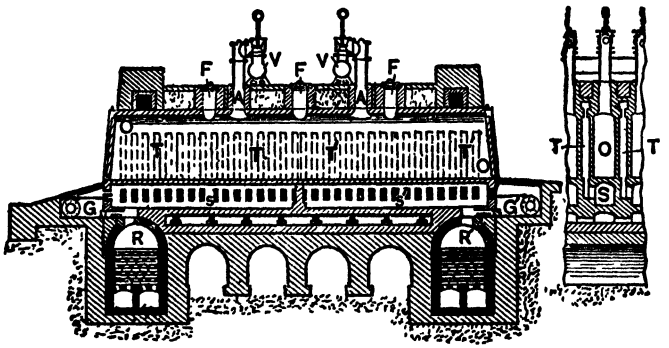


FIG. 310.—Coke-ovens.

"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. 310) 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."

If powdered petroleum coke, gas (retort) carbon, or anthracite, is mixed with soot and pitch or tar-oil, is 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 and arc lamps.

" Low temperature carbonisation " aims at treating bituminous coal at a temperature of 425°–760° C. instead of 1100°–1200° as in ordinary gas works or coke oven treatment A ton of coal then gives about 14 cwt of smokeless free burning fuel, together with 1½ gallons of crude light oil, 15–20 gallons of tar (which is different in composition from high temperature tar) and 3500–6000 cu. ft of gas of calorific value 650–800 B.Th.U. per cu ft.

CHAPTER XXXV

OXYGEN COMPOUNDS OF CARBON, ETC.

The oxides of carbon.—Three oxides of carbon, all gaseous at the ordinary temperature, are definitely known :

Carbon dioxide, 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.

Carbon Dioxide.

Carbon dioxide.—This gas, first prepared by Van Helmont about 1630, examined by Joseph Black in 1755, and more fully by Bergman (1774), was clearly recognised as an oxide of carbon by Lavoisier in 1783. Lavoisier determined its composition by burning charcoal and 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 Poison Valley (Java) and the Grotto del Cane (Naples), and the gas from such sources, as well as that collecting in cellars, which extinguishes a candle, is mentioned by Pliny. 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 it pass into the atmosphere, which 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 milky. The *fermentation* of sugar, in the preparation of beer and wine, produces carbon dioxide and alcohol : $C_6H_{12}O_6 = 2C_2H_5OH$ (*alcohol*) $+ 2CO_2$. Other kinds of fermentation and the decay of organic matter also produce carbon dioxide.

Large quantities of carbon dioxide produced by fermentation, combustion (p. 678) or from marble and acid are liquefied. 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. It is sold as "dry ice," or "drikold," for use in refrigeration

The boiling point of carbon dioxide is $-56°$ under 5·3 atm. pressure The liquid cannot exist under atmospheric pressure. The sublimation point of the solid at atmospheric pressure is $-78·52°$; a mixture of solid carbon dioxide and ether is a convenient cooling agent in the laboratory, and may be contained in a Dewar flask.

EXPT. 1.—Cut a circular groove in a large cork, 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 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.

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. 2.—Pieces of marble and dilute hydrochloric acid, in a Woulfe's bottle or Kipp's apparatus, are generally used: $CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$. 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. The gas may be dried by calcium chloride, sulphuric acid or phosphorus pentoxide.

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, boiled to free it from air, 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 : chalk, limestone, marble, *magnesia alba*, etc., give off carbon dioxide at a red heat : $CaCO_3 \rightleftharpoons CaO + CO_2$.

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, pure carbon dioxide is expelled, free from nitrogen, leaving a solution of potassium carbonate, which is used over again : $K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3$.

Properties of carbon dioxide.—Carbon dioxide is a colourless gas with a faint pungent smell and a slight acid taste. It extinguishes a burning taper, sulphur, phosphorus, etc. ; air in which a burning taper has been extinguished contains 2½ per cent. by volume of carbon dioxide ; 18½ per cent. of oxygen is still present The gas is therefore used in extinguishing fires.

EXPT. 3.—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 or bottle of sulphuric acid inside. By means of a rod attached to a knob outside, the glass tube may be broken, or by inverting the container, the acid poured from the bottle, 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 it is not poisonous and if oxygen is taken in time recovery with no ill-effect follows.

Burning sodium, potassium, and magnesium continue to burn in carbon dioxide, with separation of pure carbon :

$$4K + 3CO_2 = 2K_2CO_3 + C ;$$
$$CO_2 + 2Mg = 2MgO + C.$$

EXPT. 4.—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 Calcium carbonate dissolves in excess of carbon dioxide, but barium carbonate is insoluble.

Carbon dioxide is fairly soluble in water, which, 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 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. The gas is more soluble in alcohol than in water.

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:

$$[H] \times [HCO_3'] / [H_2CO_3] = 3{\cdot}04 \times 10^{-7} \text{ at } 18°;$$
$$[H] \times [CO_3''] / [HCO_3'] = 6{\cdot}4 \times 10^{-11} \text{ at } 25°.$$

From theoretical considerations one would expect carbonic acid to be stronger than formic acid, H·CO·OH, since the addition of a hydroxyl group, forming HO·CO·OH, should increase the acidic properties. The neutralisation of carbonic acid by alkali, with phenolphthalein as indicator, is not instantaneous as 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 Sulphur dioxide also is incompletely hydrated to H_2SO_3 in solution.

Since it dissociates in two stages, carbonic acid is dibasic 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·CO·OH ; esters of a hypothetical orthocarbonic acid, $C(OH)_4$, *e.g.*, ethyl orthocarbonate, $C(OC_2H_5)_4$, are known. 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 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:

Temperature abs	-	1000°	1500°	2000°	2500°	3000°	3500°
% dissociation	-	0 000025	0·0483	2·05	17 6	54 8	83·2

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, and 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.

About 1 gm of purified sugar-charcoal is weighed into a porcelain boat, *X*, placed inside a hard glass tube, *Y*, one half of which is packed

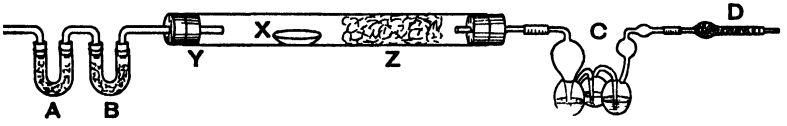


FIG. 311.—Gravimetric composition of carbon dioxide.

with recently-ignited granular copper oxide, *Z* (Fig. 311). 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*, are weighed and attached. The tube is laid 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 The oxygen is allowed to pass for a few minutes after the combustion is finished, to sweep out all the carbon dioxide, then the oxygen is displaced by air. The potash-bulbs are detached, closed with the pieces of glass rod and rubber tubing, as in the first weighing, cooled and reweighed. 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 $= x/(y - x)$.

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 weights of carbon combining with 800 parts of oxygen being as follows:

299·92 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 volumetric composition of carbon dioxide is found, approximately, in the same apparatus as was used in the case of sulphur dioxide (p. 501). A piece of pure charcoal is burnt in a confined volume of dry oxygen, over mercury. After cooling, the volume of 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 relative density of carbon dioxide is 22, hence its molecular weight is 44. This contains a molecular weight of oxygen, 32, so that the difference, 12, represents the carbon. A molecular weight of any volatile carbon compound never contains a smaller amount of carbon than 12 parts, so that 12 is the atomic weight of carbon, and the formula of carbon dioxide is CO_2.

The Atomic Weight of Carbon.—The older results from the gravimetric synthesis of carbon dioxide, corrected by Scott for the expansion of the potash solution after absorption of carbon dioxide, which alters the air displacement, are: 11·9938 (Dumas and Stas), 12·0054 (Erdmann and Marchand); 11·9973 (Roscoe); 12·0056 (Friedel); 12·0018 (van der Plaats). Newer values are 12·017 (Scott, ratio of tetramethylammonium bromide to silver); 12·005 (Richards and Hoover, ratio of Na_2CO_3 to Ag and to AgBr); 12·003 (Dean, analysis of silver cyanide and cyanate). The physical method of limiting density (p. 121) gave 12·003 (Leduc; Rayleigh; CO); 12·006 (Moles and Salazar; CO);

and 12·0039 (Baume and Perrot; CH_4). Owing to the existence of the isotope C = 13, the value is probably closer to 12·01 than to 12·00, and a value close to 12·01 was obtained by Gray and Woodhead (1933) from the limiting density of carbon monoxide

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 .

$$\begin{matrix} KO\,CO\,OK \\ KO{\cdot}CO\,OK \end{matrix} = 2K + \begin{matrix} O{\cdot}CO\,OK \\ | \\ O{\cdot}CO{\cdot}OK \end{matrix}$$

It is fairly stable at the ordinary temperature when dry, but is decomposed by water with evolution of oxygen. The sodium salt can be prepared by electrolysis at 0° of a solution of 60 gm. of sodium carbonate per litre By the action of hydrogen peroxide on sodium carbonate a crystalline salt is obtained, which was formerly considered to have the composition $Na_2CO_4 + \frac{1}{2}H_2O_2 + H_2O$, but is a carbonate containing hydrogen peroxide of crystallisation (p. 300) : $Na_2CO_3 + 1\frac{1}{2}H_2O_2$

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, are said 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, and **permonocarbonic acid,** corresponding with Caro's acid, respectively .

percarbonic acid

permonocarbonic acid

By the action of phosphoric acid on potassium percarbonate in ether, an unstable solution of percarbonic acid, $H_2C_2O_6$, is said to be 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, $K_2O,Al_2O_3,6SiO_2$, 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): $K_2O,Al_2O_3,6SiO_2 + CO_2 + 2H_2O = K_2CO_3 + Al_2O_3,2SiO_2,2H_2O + 4SiO_2$

The 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.

Photosynthesis.—Green plants contain a pigment known as **chlorophyll**, 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 given out 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 tissues are built. It is converted in the leaves, under the action of light, into **carbohydrates**. The net result of this change may be represented by the equation:

$$xCO_2 + xH_2O + \text{energy of light} = (CH_2O)_x \text{ (sugars)} + O_2$$

The production of oxygen from carbon dioxide by the agency of living green plants under the influence of light was observed by Priestley, Ingen-Houss and Senebier, at the close of the eighteenth century. By the activity of green plants and marine organisms, therefore, the carbon dioxide content of the atmosphere tends to be reduced.

EXPT 5.—Watercress or mint is put into a flask filled with tap water and provided with an arrangement for collecting gas. On exposure to bright sunlight if available, otherwise to bright daylight, bubbles of gas are produced on the leaves, which rise into the test-tube (Fig 312) These consist largely of *oxygen*.

FIG. 312.—Production of oxygen from carbon dioxide by green plants in light

The influence of light in promoting chemical changes was met with also in the union of hydrogen and chlorine. In some cases the invisible ultra-violet rays of the spectrum are most active, and the violet end of the spectrum 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 666mμ

Hydrogen sulphide 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 is retarded by violet light, but accelerated by red light

The oxygen absorbed by the plant furnishes nearly all 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 given off.

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, calcium nitrate, ammonium sulphate, blood, guano, and other nitrogenous animal products, and farmyard manure. It is in all cases converted into nitrates before assimilation by the activity of micro-organisms in the soil. 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, boron, 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.

Respiration.—We now consider those processes which tend to increase the atmospheric carbon dioxide. Early experimenters, such as Mayow, Scheele, Priestley, and Lavoisier, were aware of the 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 blood contains red corpuscles, composed of protoplasm with a colouring matter known as **hæmoglobin**; the latter contains iron in the form of a coloured compound **haematin**, $C_{34}H_{33}N_4FeO_5$, associated with a protein. Haemoglobin 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 expansion and contraction of the lungs, by which respiration occurs, are brought about by movements of the diaphragm and the ribs, both of which are co-ordinated 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 daylight activities of plants, absorbing carbon dioxide from the atmosphere, retaining the carbon and giving out the oxygen, and the respiratory functions shared by them in

common with all living organisms, absorbing oxygen and giving out 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 0·04–0·3 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 ($1·62 \times 10^9$ 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

Carbon Monoxide.

Carbon monoxide.—Lassone (1776) obtained an inflammable gas by heating charcoal with zinc oxide; Priestley (1796) substituted iron-scales (Fe_3O_4) for zinc oxide, and 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. It is also formed in the combustion of petrol in automobile engines, the exhaust gases of which are very poisonous

The production of carbon monoxide in a fire is usually 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 Dixon and H B. Baker, however, consider that carbon monoxide is 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 below 800°, but above 1000° it is fairly rapid The 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 The amount of carbon monoxide formed in equilibrium increases with the temperature.

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 air was noticed by Macquer in 1771; large quantities of carbon monoxide are formed when a blast of air is forced

through incandescent coke. 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. 6.—Pass a slow current of carbon dioxide over pieces of charcoal heated to bright redness in an iron tube (Fig. 313). The

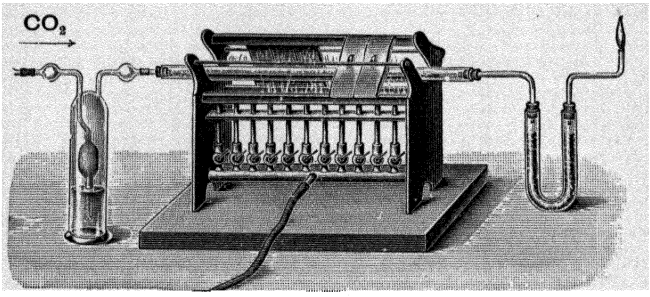


FIG. 313.—Carbon monoxide **from carbon** dioxide and carbon.

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 $4K + 3CO_2 = 2K_2CO_3 + C$.

Preparation of carbon monoxide.—Carbon monoxide is produced on the large scale by passing carbon dioxide over heated carbon; 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 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. A mixture of 85 parts of phosphorus pentoxide and 15 of water may be used with formic acid (Thompson, 1929).

EXPT. 7.—Concentrated sulphuric acid is heated to 100° in a flask, and concentrated formic acid dropped in from a tap-funnel. Cold concentrated sulphuric acid may also be dropped on dry sodium

formate in a flask. The gas is washed with caustic soda; if required pure, it is dried with phosphorus pentoxide and collected over mercury
Note: *carbon monoxide is very poisonous*

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 removed by washing with caustic soda.

EXPT 8.—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. This is passed through a wash-bottle containing caustic soda solution, and the carbon monoxide collected over water.

Potassium ferrocyanide on heating with ten times its weight of concentrated sulphuric acid in a large flask, evolves nearly pure carbon monoxide, except in the later stages of the reaction, but the reaction is usually somewhat violent:

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

Carbon monoxide is produced by withdrawing the elements of water from formic acid by the catalytic action of metallic rhodium. The reverse reaction, *i.e.*, the synthesis of formic acid, is effected by 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. It is not poisonous to green plants or soil bacteria, which oxidise it.

The poisonous action of carbon monoxide depends on the absorption of the gas by the haemoglobin of the blood, forming bright-red **carboxy-haemoglobin**, which is a very stable substance, not decomposed by oxygen. 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 $-138{\cdot}7°$, and the critical pressure is 34·6 atm. The liquid boils at $-191{\cdot}5°$ 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; 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 14 and the molecular weight 28 (approximately). The moist 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: $Ni(CO)_4$, $Fe(CO)_4$, $Fe(CO)_5$, $Fe_2(CO)_9$, $Co(CO)_3$, $Co_2(CO)_8$, $Mo(CO)_6$, $Ru(CO)_2$ 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. It 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, *e.g.*, in the blast furnace. It reduces iodine pentoxide at 90°, with liberation of iodine: $I_2O_5 + 5CO = I_2 + 5CO_2$, a reaction which is used for the estimation of carbon monoxide in gases. A mixture of carbon monoxide and hydrogen may be analysed in this way. If a mixture of carbon monoxide and methane is passed over copper oxide at 300°, only the carbon monoxide is oxidised. When a gas containing only 0·05 per cent. of CO is shaken with a solution of palladious chloride, a black precipitate of palladium is produced.

A mixture of two volumes of carbon monoxide and one volume of oxygen explodes on ignition. 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, which has been dried with phosphorus pentoxide, is extinguished when plunged into a jar of oxygen containing concentrated sulphuric acid which has been standing for a few hours carefully stoppered.

Girvan (1903) found 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. According to W. A. Bone and Weston (1926), a very dry mixture is exploded by a very powerful electric spark.

The catalytic influence of moisture in this (and other similar) reactions is still somewhat obscure Since carbon monoxide readily reduces steam at high temperatures $CO + H_2O \rightleftharpoons CO_2 + H_2$, Dixon supposed 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 effects of moisture.—Numerous cases of the catalytic effect of moisture are known Dry chlorine does not combine with many 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 Nitric oxide and oxygen, hydrogen and chlorine, and ammonia and carbon dioxide, do not react when very pure and dry. Sodium, potassium, and phosphorus scarcely react with dry oxygen, although dry boron, tellurium, arsenic and antimony react readily under the usual conditions

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 H E Armstrong's theory (1885), too pure to form an electrically-conducting circuit, which he considers necessary for chemical change

CO	O H_2	O		CO_2	H_2O
CO	O H_2	O		CO_2	H_2O
Before				After	

The water normally forms a "closed conducting circuit," owing to traces of impurity, and the oxygen acts as a depolariser.

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 314). 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*.

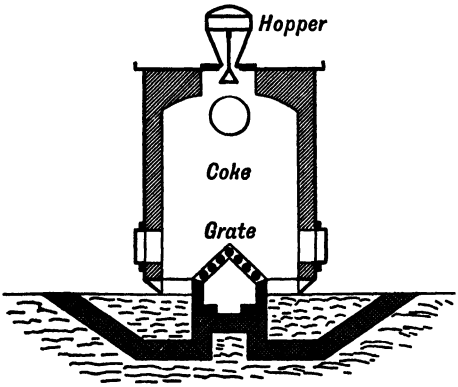


FIG 314.—Gas producer.

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) $C + 2H_2O \rightleftharpoons CO_2 + 2H_2$. 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	1·05	0·975
1125	99·4	50·9	48·5	0 6	80·8	1 05	0·988

Average water gas has the following composition by volume: H_2, 49·17; CO, 43·75; CO_2, 2·71; methane, 0·31; N_2, 4·00. Its calorific value 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 it is shut off, and an *air blast* turned on until the fuel is again heated to bright redness The gas formed in the air-blow is usually turned to waste. 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, which is short (say two minutes, to eight minutes of steam-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 **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

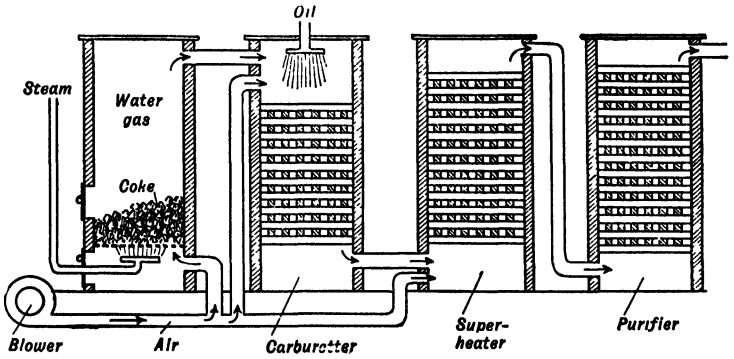


FIG 315 —The manufacture of carburetted water gas

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 (Fig. 315). 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 vapour 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 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
,, 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 value of producer and semi-water gas is low, being usually about 125 B Th U. per cu. ft, as compared with about 600 for good coal gas and 350 for water gas.

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 ($C + H_2O \rightleftharpoons CO + H_2$) 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.

Carbonyl chloride, or phosgene.—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 *gennao*, 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. 8·2°. 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 :

$$CO\begin{matrix}Cl\\Cl\end{matrix} + \begin{matrix}H\cdot OH\\H\cdot OH\end{matrix} = CO\begin{matrix}OH\\OH\end{matrix} + 2HCl = CO_2 + H_2O + 2HCl.$$

Phosgene is, therefore, the chloride of carbonic acid. When the gas is passed into a solution of ammonia in toluene, urea is formed · $COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl$. Both urea and ammonium chloride are precipitated, but may be separated by warming with alcohol, in which urea is soluble. The alcoholic solution deposits crystals of urea on evaporation and cooling.

The amide of carbonic acid, $HO\,CO\,NH_2$, is called **carbamic acid.** Its ammonium salt, $NH_4O{\cdot}CO{\cdot}NH_2$ is contained, together with ammonium bicarbonate, NH_4HCO_3, in commercial "carbonate of ammonia"

Carbonyl bromide, $COBr_2$, is slowly formed from carbon monoxide and bromine vapour

Carbonyl sulphide, or carbon oxysulphide.—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 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 first formed is hydrolysed by water · $HCNS + H_2O = COS + NH_3$ The gas 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 trimethyl phosphine, $P(CH_3)_3$, pyridine, and nitrobenzene

Carbonyl sulphide is a colourless odourless gas, moderately soluble in water, readily soluble in toluene It liquefies at 0° under 12·5 atm pressure, b pt. −50·2°; m. pt. −138·2°. 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, but not after drying with phosphorus pentoxide. $2COS + 3O_2 = 2CO_2 + 2SO_2$ A heated platinum spiral decomposes the gas without change of volume into sulphur and carbon monoxide: $COS = CO + S$ (solid); the reaction $2COS = CS_2 + CO_2$ also occurs.

The aqueous solution of carbonyl sulphide is slowly hydrolysed $COS + H_2O \rightleftharpoons HO{\cdot}CO\,SH \rightleftharpoons CO_2 + H_2S$ The intermediate substance, $HO{\cdot}CO{\cdot}SH$, is **thiolcarbonic acid.** 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.—At 120°, under 3 to 4 atm. pressure, carbon monoxide is rapidly and completely absorbed by a concentrated solution of caustic soda, **sodium formate** being produced. $NaOH + CO = H{\cdot}COONa$. From this, anhydrous formic acid, $H{\cdot}COOH$, 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 is distilled.

Formic acid is a colourless liquid with a pungent odour, sp. gr. 1·226, b. pt. 100·6°, m. pt. 8·43°. It acts violently on the skin, raising blisters. The acid is contained in red ants (*Formica rufa*),

and was first obtained from them by distillation by Samuel Fisher, whose results were published by John Ray in 1671. 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 at 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 CO CO_2H, and finally **glycollic acid**, $H_2(OH)C\ CO_2H$, are obtained in large quantities. All these compounds, therefore, may be obtained directly from carbon monoxide

Carbon suboxide.—If **malonic acid**, $CH_2(COOH)_2$, or ethyl malonate, $CH_2(COOC_2H_5)_2$, is treated with a large excess of phosphorus pentoxide at 300° under 12 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 $CH_2(COOC_2H_5)_2 = C_3O_2 + 2H_2O + 2C_2H_4$

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.—Sulphur vapour when passed over red-hot carbon produces carbon disulphide, CS_2, a volatile liquid. The reaction is endothermic and reversible: $C + 2S \rightleftharpoons CS_2 - 19{\cdot}0$ k. cal. Carbon disulphide was discovered by Lampadius in 1796, by heating pyrites with charcoal.

A vertical cast-iron or fireclay retort, set in a furnace, is filled with charcoal Sulphur is fed in through a side tube at the base of the retort, being kept fused by the waste heat. The sulphur volatilises,

and the vapour passes over the charcoal at 800°-900°, forming carbon disulphide. The vapours pass through a small iron cylinder, where sulphur is deposited, and the carbon disulphide is condensed in a very long worm-tube cooled by water.

In Taylor's electrical process (1899), used in America, a tower 40 ft. high and 16 ft. in diameter (Fig. 316) 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.

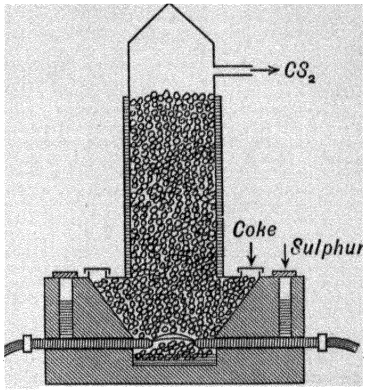


FIG. 316.—Taylor's electric carbon disulphide furnace.

Carbon disulphide is purified by distillation over lead acetate; or by agitation with mercury until it no longer blackens it, after which it is redistilled over white wax and then over phosphorus pentoxide.

On the small scale, carbon disulphide can be prepared as follows. A combustion tube is packed with recently ignited charcoal, and the

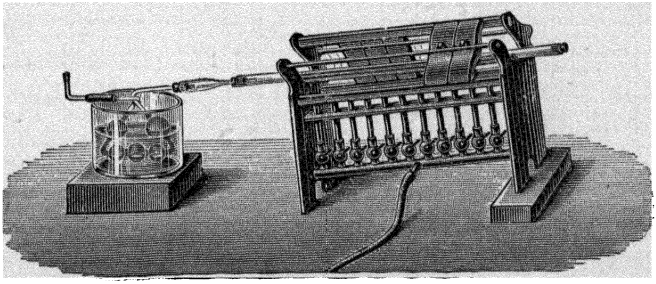


FIG. 317.—Preparation of carbon disulphide.

lower end is connected with bulb tubes surrounded by ice (Fig. 317). The tube is heated to redness and 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 is collected in the bulbs.

Properties of carbon disulphide.—Carbon disulphide is a colourless, mobile, strongly refracting liquid, which boils at 46·25°, solidifies at −116°, and remelts at −112°. Its density at 0° is 1·2923.

100 c.c. of water dissolve 0·204 gm of CS_2 at 0°, 0·179 at 20°, and 0·014 at 49°. Carbon disulphide mixes with absolute alcohol, ether, and oils It also dissolves sulphur, white phosphorus, indiarubber, camphor, resins, etc., and is used as a solvent. Carbon disulphide readily volatilises Its vapour has usually an exceedingly unpleasant odour which is removed by careful purification, when the liquid smells of chloroform, but the smell soon becomes unpleasant again. The vapour has a relatively low ignition temperature: a test-tube filled with hot oil held over the liquid in a dish sets fire to the vapour The vapour explodes with air or 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.

Carbon disulphide, being an endothermic compound, is unstable. 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.

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:

$$CS_2 + 3Cl_2 = CCl_4 \text{ (b. pt. 77°)} + S_2Cl_2 \text{ (b pt. 138°)}$$

Both products of this reaction are useful, and are separated by fractional distillation. Carbon tetrachloride is used as a grease solvent, and under the name of *pyrene* for extinguishing fires (*not sodium !*).

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 nickel at 450°, yields hydrogen sulphide:

$$CS_2 + 2H_2 = C + 2H_2S.$$

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 a solution of triethyl phosphine, $P(C_2H_5)_3$, in ether, forming a red crystalline compound $P(C_2H_5)_3.CS_2$

When the vapour of carbon disulphide is passed over red-hot copper, carbon is deposited and copper sulphide formed $CS_2 + 4Cu = C + 2Cu_2S$. In this way the composition of the substance was first determined by Vauquelin A mixture of the vapour with steam or hydrogen sulphide, 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 elements (Berthelot, 1856.)

Carbon subsulphide.—This compound, C_3S_2, corresponding with the suboxide C_3O_2, was discovered by Lengyel (1893) 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, or a zinc anode. $3CS_2 + 4Zn = C_3S_2 + 4ZnS$. The liquid is distilled *in vacuo* and the vapour condensed at $-40°$ A yellowish-red solid is formed, m. pt $-0{\cdot}5°$. 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 bromide, $C_3S_2Br_6$, formed directly, 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 $73{\cdot}5°$ with slight decomposition, has a very offensive odour, and is slowly hydrolysed by water When treated with nickel carbonyl, solid $(CS)_x$ is said to be 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.—Carbon disulphide when agitated with a concentrated solution of caustic soda slowly dissolves, forming sodium carbonate and **sodium thiocarbonate,** Na_2CS_3, which may be regarded as the carbonate in which oxygen is replaced by sulphur (Berzelius, 1826): $3CS_2 + 6NaOH = 2Na_2CS_3 + Na_2CO_3 + 3H_2O$.

If a solution of sodium sulphide is used instead of caustic soda, the reaction is more rapid, and sodium thiocarbonate alone is formed: $Na_2S + CS_2 = Na_2CS_3$ The pure salt is obtained by adding CS_2 to an alcoholic solution of NaHS. On adding ether, pinkish-yellow crystals, Na_2CS_3,H_2O, of the thiocarbonate separate. A deep red solution and yellow crystals of ammonium thiocarbonate, $(NH_4)_2CS_3$, are formed when carbon disulphide and concentrated ammonia are allowed to stand together for a few days.

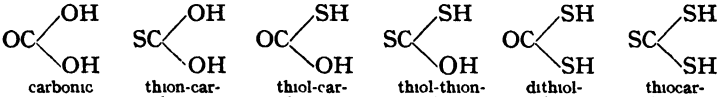
Free **thiocarbonic acid,** H_2CS_3, is obtained as a bright red liquid by dropping crystals of $(NH_4)_2CS_3$ into a large excess of concentrated hydrochloric acid. **Ammonium perthiocarbonate,** $(NH_4)_2CS_4$, is obtained together with the thiocarbonate by refluxing $(NH_4)_2S_5$ solution with carbon disulphide; prolonged action gives orange-yellow crystals of

$(NH_4)_2CS_3$, but incomplete action gives yellow crystals of $(NH_4)_2CS_4$, which are washed with carbon disulphide and ether On adding this salt to 98 per cent. formic acid, **perthiocarbonic acid**, H_2CS_4, not quite pure, is formed. With hydrochloric acid only H_2CS_3 and sulphur are formed. (Mills and Robinson, 1928)

Thiocarbonates are used in destroying *Phylloxera*, a kind of aphid infesting vines. Carbon disulphide is a poison for this insect, 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 $SC(SK)(OC_2H_5)$, known as **potassium xanthate**, is formed. It is decomposed by acids, with liberation of carbon disulphide and alcohol, C_2H_5OH, 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:



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

Cyanogen.—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**, probably a polymerised form of cyanogen, $(CN)_n$; it decomposes slowly into cyanogen at 800°. 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. 9.—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.*

An economical method for the preparation of cyanogen (which is not pure, but contains some carbon dioxide and hydrocyanic acid) 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 quickly decomposes with evolution of cyanogen gas, forming 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 :

$$2CuCN + 2FeCl_3 = 2CuCl + 2FeCl_2 + C_2N_2.$$

Cyanides are produced by the action of nitrogen on carbides at high temperatures : if nitrogen is passed over barium carbide, or an intimate mixture of barium oxide and carbon, at a red heat, **barium cyanide** is produced : $BaO + 3C + N_2 = Ba(CN)_2 + CO$. Cyanogen is present in blast-furnace gas in small quantities.

Properties of cyanogen.—Cyanogen is a colourless gas, soluble in 4 vols of 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 $-20{\cdot}7°$, which freezes below $-35°$ to a white solid, melting at $-27{\cdot}92°$. The density of the gas shows that it has the formula C_2N_2. It is an endothermic compound : $2C\ (\text{graphite}) + N_2 = C_2N_2 - 70$ k. cal.

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, 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 formed : $KCN \rightleftharpoons K^{\cdot} + CN'$.

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.

$$\begin{array}{l} CN \\ | \\ CN \end{array} \xrightarrow{H_2O} \begin{array}{l} CONH_2 \\ | \quad \text{(oxamide)} \\ CONH_2 \end{array} \xrightarrow{H_2O} \begin{array}{l} COOH \\ | \quad \text{(oxamic acid)} \\ CONH_2 + NH_3 \end{array} \xrightarrow{H_2O} \begin{array}{l} COOH \\ | \quad \text{(oxalic acid)} \\ COOH + NH_3 \end{array}$$

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, the monoxide is burnt to carbon dioxide.

The formula of cyanogen may be written as N·C·C·N, with tervalent nitrogen, as is shown by its reduction to ethylenediamine, $H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$.

Hydrocyanic acid.—When potassium cyanide 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 25° and freezing at −15°, collects. This is anhydrous hydrocyanic acid. The vapour burns with a purple flame in air. The anhydrous acid is best produced by passing pure hydrogen sulphide slowly over dry mercuric cyanide 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: $C_2H_2 + N_2 = 2HCN$; when a mixture of nitrogen, methane, and hydrogen is passed through a carbon arc $2CH_4 + N_2 = 2HCN + 3H_2$, and, according to Scheele, when ammonia gas is passed over strongly heated charcoal.

Anhydrous hydrocyanic acid is a really dangerous poison; its preparation should be undertaken only by an expert chemist. A dilute solution may be prepared by distilling potassium ferrocyanide with dilute sulphuric acid (1 acid + 2 water); the 2½ 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.

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, although larger doses are almost instantaneously fatal. The best antidote is said to be ferrous hydroxide, obtained by adding 1·5 gm. of caustic soda in 300 c.c. of water and 2 gm. of magnesia to 7·5 gm. of ferrous sulphate crystals in 300 c.c. of water.

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: $CN' + H_2O \rightleftharpoons HCN + OH'$.

Although organic derivatives with structures $R{-}C{\equiv}N$ (cyanides), and $R{-}N{\rightleftharpoons}C$ (isocyanides) are isomeric, the cyanide ion from the two corresponding acids is identical, $[:N:::C:]'$.

Cyanogen Chloride.—If chlorine is passed into aqueous hydrocyanic acid, cyanogen chloride, CN Cl, is formed, which may be condensed in a freezing mixture to a colourless mobile liquid, b pt. 12·7° (Berthollet, 1787) The liquid if slightly acidified, rapidly polymerises to a 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,** $CN{\cdot}NH_2$

Cyanogen chloride is best prepared by acting on sodium cyanide, a little water, and carbon tetrachloride, with chlorine gas and distilling It is used in place of hydrocyanic acid for fumigation, since it is lachrymatory and is easily detected

Bromine reacts with hydrocyanic acid or potassium cyanide to form white crystalline **cyanogen bromide,** $CN{\cdot}Br$, iodine reacts with potassium cyanide to form **cyanogen iodide,** CN I. The latter may occur 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 boiling 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,** 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.

Cyanates.—Potassium and sodium cyanides, in a state of fusion, are powerful *reducing agents*· 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: $HCNO + H_2O = NH_3 + CO_2$.

Pure cyanic acid is a colourless liquid obtained by heating crystalline **cyanuric acid,** $(CNOH)_3$, obtained by distilling urea.

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 Wohler 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 one of convenience. Previously to Wöhler's discovery, urea had been obtained by John Davy in 1811, from phosgene and ammonia, but he was not aware of the nature of the products of the reaction.

Flame.

Flame.—A flame is a zone in which chemical reaction 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 produced in chemical reactions only 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. The glow of phosphorus is a familiar example and there are many others. 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. 10.—Thirty c c of 30 per cent. hydrogen peroxide are added in a dark room 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. 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. 11.—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. 12.—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. 13.—Stretch a piece of fine wire gauze over a funnel, and place a *small* heap of gunpowder in the centre of it (Fig. 318). Pass a rapid stream of coal gas through the funnel, and ignite the gas from above. The powder remains in the centre of the flame without explosion. If the flame is slowly turned down, the gunpowder ignites.

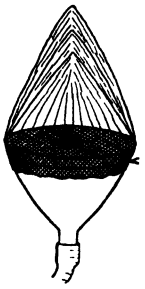


Fig. 318.—Experiment to demonstrate that a flame is hollow.

Expt. 14.—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 relative, and depend on which gas is inside and which outside the flame. This has already been illustrated in the cases of oxygen and hydrogen and hydrogen and chlorine.

Expt. 15.—A lamp chimney with a tinplate top (Fig. 319) is fitted with a cork at the lower end, through which pass a straight tube and a narrower tube bent at an angle Coal gas is passed in through the bent tube, and may be kindled at the top of the glass. At the same time, air is drawn in through the wider 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 a taper is 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.

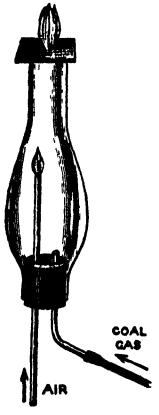


Fig. 319.—Air burning in coal gas.

If the supply of coal gas is gradually reduced, the upper flame shrinks and becomes less luminous, whilst the lower flame increases in size, due to the circumstance that the oxygen has now a more limited supply of coal gas available, and the combustion extends 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. 16.—Arrange a lamp chimney with two tubes as shown in Fig 320. Pass coal gas 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 reacting with the unburnt gas in the centre of the large hollow flame

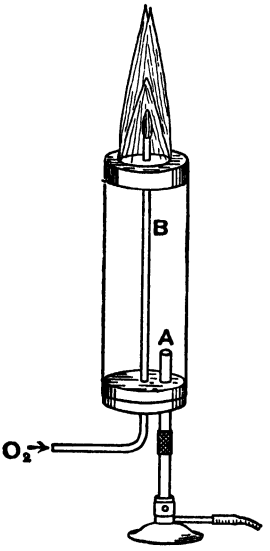


FIG. 320.—Oxygen burning inside a coal gas flame

An 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 combustible material. The liquid oil or melted wax rises in the 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. 17.—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 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 owing to its capillary structure, and it prevents too rapid conduction of heat away from the heated point where distillation occurs.

The structure of flame.—A **hydrogen flame** burning in air or oxygen consists (Fig. 321) of *two* cones, an inner one, *A*, of unburnt gas, and an outer, *B*, in which the single chemical reaction $2H_2 + O_2 = 2H_2O$ is occurring with evolution of heat and light. The **flame of ammonia** burning in oxygen consists, however, of *three* cones, an inner, *A* (Fig. 322), 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 **hydrogen sulphide, cyanogen,** or **carbon disulphide** vapour in oxygen or air is similar: with cyanogen the cone *B* is pink in colour and corresponds with the reaction: $C_2N_2 + O_2 = 2CO + N_2$, whilst the cone *C* is greenish and represents complete combustion of the carbon monoxide.

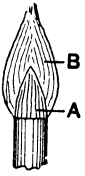


FIG. 321.—Structure of hydrogen flame (two cones).

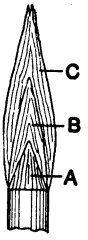


FIG. 322.—Structure of carbon disulphide or ammonia flame (three cones).

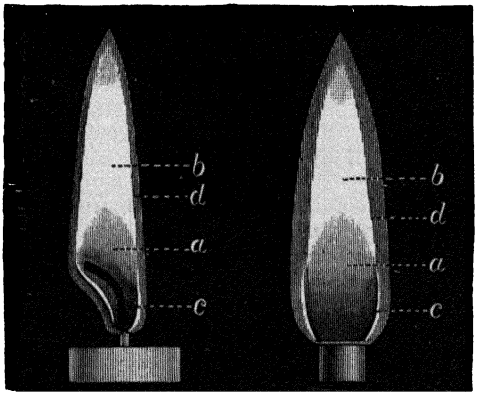


FIG. 323.—Structure of hydrocarbon flames.

Hydrocarbon flames are more complicated, and contain *four* regions first defined by Berzelius. The flame of a candle or of coal gas burning at a jet (Fig. 323), 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-visible outer mantle, completely surrounding the flame. 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. 324). The regions *a* and *d* remain.

FIG. 324.—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 example, luminous, whilst those of hydrogen and carbon monoxide are non-luminous? There are two principal theories to account for the luminosity of flame:

(1) **Davy's theory** (1816), which ascribes the luminosity to particles of *solid carbon* produced by the thermal decomposition of the combustible body and heated to incandescence in the flame.
(2) **Frankland's theory** (1861), according to which the luminosity is due to incandescent *vapours of dense hydrocarbons* in the flame.

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 fire-damp explosions in coal mines, which were prevalent when open candle flames were used. These are caused by the ignition of mixtures of methane (*fire-damp*) and air, or, as we now know, sometimes by the kindling of a mixture of very fine coal-dust itself with air. Davy soon found that if a flame is cooled it is extinguished, and he recognised that combustible gases have different **ignition points.**

EXPT 18.—Lower a close spiral of thick copper wire over a candle flame: the latter is extinguished.

EXPT. 19.—(i) Depress a piece of fine wire gauze over a Bunsen flame. The flame at first does not pass through owing to the cooling caused by conduction of heat through the metal gauze, and a red-hot ring is seen with a dark centre corresponding with unburnt gas in the centre of the flame. This gas is passing through the gauze, as 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.

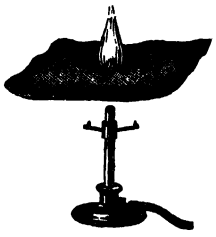


FIG. 325.—Principle of safety lamp.

(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. 325). This flame, in which air is mixed with gas before combustion, is blue and non-luminous.

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. 326). 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 outside because the heat is conducted away by the gauze. The gauze may even become red hot from the gas burning inside, but as the ignition temperature of methane is high, the flame does not pass through to the 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. 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.

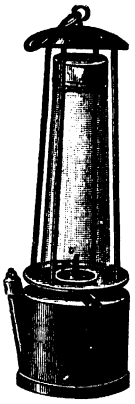


FIG. 326.—Davy's safety lamp.

EXPT. 20.—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. 19 was due, according to Davy, to the carbon particles burning as fast as produced in the oxygen supplied.

Flames known to contain solid particles, such as those of zinc, magnesium and potassium in oxygen, are very luminous, and the presence of solid particles of carbon in luminous hydrocarbon flames is proved by the fact that a powerful beam of light is reflected by such a flame, and the reflected light is polarised. The presence of carbon particles is also made probable by the following experiments:

EXPT. 21.—Hold a cold piece of pipeclay tube in a candle flame. Carbon is deposited on the lower part only, not on the top.

EXPT. 22.—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. 327), render the flame luminous.

Faraday accepted Davy's views, but instead of supposing that the carbon arose from the decomposition of the gas by heat, he put forward the erroneous 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 (p 664) that if methane or ethylene is exploded with a deficiency of oxygen, all the carbon is burnt to carbon monoxide, whilst the whole or part of the hydrogen is set free · $C_2H_4 + O_2 = 2CO + 2H_2$. Faraday's theory is untenable.

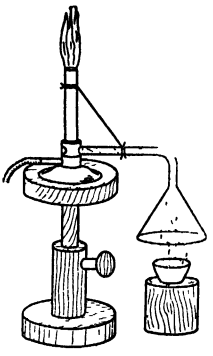


FIG 327 —Bunsen flame rendered luminous by smoke from burning camphor

EXPT 23 —The structure of a candle flame is shown by an experiment due to Faraday. A bent glass siphon is lowered into the flame (Fig. 328). With the tube just above the wick, dense white vapours pass over into the flask · these correspond with the first process in the flame, the volatilisation of the solid wax on the wick by the heat in 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.

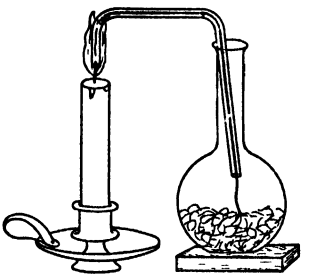


FIG. 328.—Faraday's experiment to illustrate the structure of a candle flame.

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 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 exhausted 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 flames of phosphorus and 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, although only 1·41 per cent of these hydrocarbons were present Lewes assumed that hydrocarbons are decomposed by heat, with the intermediate formation of acetylene. $2CH_4 = C_2H_2 + 3H_2 = 2C + 4H_2$. 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 and diminishes in size when a large supply of air is admitted and the flame "roars" (as in the Téclu burner); (2) a still paler blue outer cone, which remains constant in size. 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 and hydrogen, which burn in the outer cone.

EXPT. 24.—The effect of admixture of air on the flame of a combustible gas may be studied with the apparatus shown in Fig. 329, 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

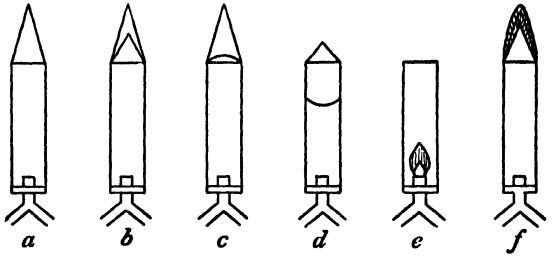


FIG. 329.—Smithells's experiments on flames.

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 flame.**

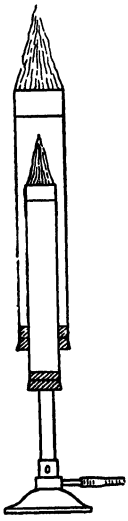


FIG 330.—Smithells's flame-cone separator.

EXPT 25.—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. 330) of one glass tube sliding inside a wider tube A mixture of air and coal gas from a Bunsen burner is passed into the central tube The central position of the inner tube may be kept 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

By analysing the gas from the space between the two cones, it was found to consist of nitrogen, carbon monoxide, carbon dioxide, steam and hydrogen. The composition of the mixture was the

same if pure methane containing no hydrogen was 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, and with excess of oxygen, when some carbon dioxide is formed, an equilibrium, $CO + H_2O \rightleftharpoons CO_2 + H_2$, is set up, 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 Horstmann in 1877-79, and by Dixon in 1884; Smithells, and later Haber, found that it 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 found (Féry, 1904, etc)

Bunsen, fully aerated	1871°	Oxy-coal-gas blowpipe	2200°
,, insufficient air	1812°	Oxy-hydrogen blowpipe	2420°
,, acetylene	2548°	Oxy-acetylene explosion	3000°–4000°
,, alcohol	1826°	[Electric arc	3760°]
Alcohol flame	1705°	[Sun	7800°]
Hydrogen, free flame	1900°		

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. 26.—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 gradually admit carbon dioxide: the flame becomes blue and non-luminous, but consists of only *one* cone instead of two, as in the ordinary Bunsen flame.

Lewes states that 1 volume of ordinary coal gas requires the following proportions by volume of gases to render it non-luminous: CO_2, 1·26; N_2, 2·30; CO, 5·11; H_2, 12·4; air, 2·27; O_2, 0·5. That the effect cannot be due entirely to cooling is evident from the effect of carbon monoxide, which gives a hotter flame than coal gas.

(3) **Cooling**: Wibel showed that cooling the flame resulted in loss of luminosity.

EXPT. 27.—Bring a cold flat-iron in contact with the flame of coal gas burning at a fishtail burner. The flame loses its luminosity.

EXPT. 28.—Suspend a platinum crucible in a Bunsen flame which has been rendered just luminous by adjusting the air-holes when the crucible is red hot. Now pour cold water in the crucible; the flame loses its luminosity.

If a platinum tube is fitted to the top of a Bunsen burner, the flame lighted at the top becomes luminous when the platinum tube is heated to redness by a blowpipe flame. This result, however, is probably due to the formation of acetylene 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. 29.—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. 331). On turning down the gas, the flame strikes back, *i.e.*, flashes down the tube.

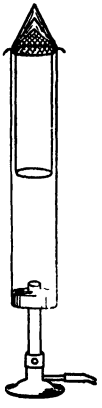


FIG. 331.—Separation of cones of bunsen flame.

If the air supply is slowly increased, the inner cone of the flame passes down separately, and 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.

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. 29, 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 to 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 in m. per sec.

$8H_2+O_2$	3535	$C_2N_2+O_2$	2728
$2H_2+O_2$	2821	H_2+Cl_2	1729
H_2+3O_2	1712		

In many cases the velocity of the detonation wave is approximately twice that of the propagation of sound through the burnt gas heated to the temperature of combustion under the conditions of experiment.

The increased violence of the combustion and the great speed of propagation of the flame when the detonation wave has been established, may be demonstrated by the following experiments:

EXPT. 30.—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. Drain any water from the tubes, 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 A strong glass screen should be placed before the lower part of the tube.

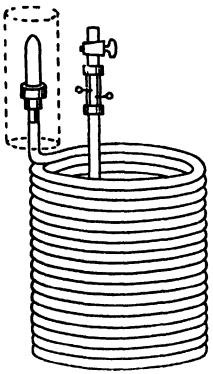


FIG. 332.—Velocity of detonation wave.

EXPT. 31.—A coil of lead piping, 30 ft. long and ¼ 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, by Faraday's cement, a strong glass tube with firing-wires sealed through the glass and a brass stopcock above (Fig 332). 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 test-tube is shattered at the same instant as the flash is seen in the firing tube. The mixture $2CO+O_2$ burns in a test-tube without explosion.

CHAPTER XXXVI

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.

Boron.

Boron.—The salt **borax**, $Na_2B_4O_7,10H_2O$, has been known from fairly early times; it was brought from Tibet, called *tincal*, was used as a flux in metallurgy, and is mentioned by Geber. In 1702 Homberg obtained a crystalline substance by distilling green vitriol with borax; this was known as *sal sedativum*. Baron (1747) showed that Homberg's "salt" has acidic properties, since when treated with soda borax is formed. It was called **boracic acid**, or **boric acid**; Lavoisier suggested that it consisted of oxygen united with an unknown radical, a peculiar element later called 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 by the second method was repeated on a larger scale by Gay-Lussac and Thenard (1808), who described the properties of the element.

Borax.—Most of the borax of commerce is prepared from the natural borax of Lake Borax and from Searle's Lake, in California, which contain one or two ounces of borax per gallon, or from minerals such as *colemanite*, $Ca_2B_6O_{11},5H_2O$, in Asia Minor and America; *boracite*, $2Mg_3B_8O_{15},MgCl_2$, at Stassfurt; and *boronatrocalcite*, $CaB_4O_7,NaBO_2,8H_2O$, in Chile.

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 hot solution, above 60°; 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 561° to a transparent glass. Borax is slightly hydrolysed in solution, and since boric acid, H_3BO_3, is very weak, 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, in preparing glazes, as a flux in soldering, in making optical and hard glass, 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).

Boric acid.—Boric acid is produced from borax by treating it with a mineral acid. It is sparingly soluble in cold water, but more readily in hot water: 1·95 gm. at 0°, 2·92 gm. at 12°, and 16·82 gm. at 80°, in 100 c.c. of water. It is less soluble in solutions of acids.

EXPT. 1.—To a hot saturated solution of borax add concentrated hydrochloric acid till the solution is strongly acid to litmus. On cooling, scaly six-sided crystals of boric acid (Fig. 333) separate $Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$. Wash the crystals with cold water, and recrystallise from hot water.

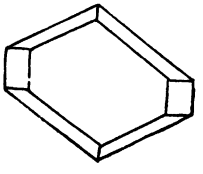


FIG. 333.—Crystal of boric acid.

In the volcanic regions of Tuscany, jets of steam called *soffioni* escape from the ground, and are surrounded by lagoons; these jets contain steam, carbon dioxide, hydrogen sulphide, nitrogen, ammonia, and traces of boric acid, which is volatile in steam. The boric acid of *soffioni* may have been produced by the action of superheated water on boron nitride: $BN + 3H_2O = H_3BO_3 + NH_3$, or on tourmaline, which contains 3–4 per cent. of B_2O_3 and is found *in situ*. In the recovery of the boric acid, a basin is built around two or three of the *soffioni*, 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. 334), 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, pearly white monoclinic or triclinic crystals with a greasy feel. On heating at 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 high temperature 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:

$$4H_3BO_3 = 4HBO_2 + 4H_2O = H_2B_4O_7 + 5H_2O = 2B_2O_3 + 6H_2O.$$

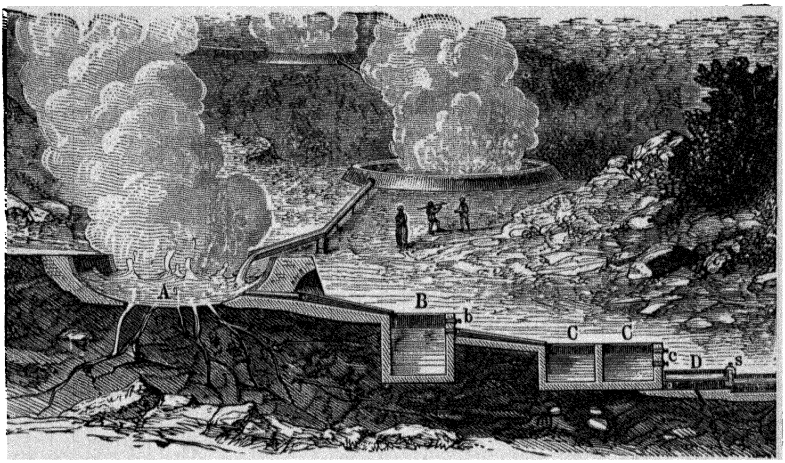


FIG. 334.—Boric acid lagoons.

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 also 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: $Na_2B_4O_7 + BaCl_2 + 3H_2O = Ba(BO_2)_2 + 2H_3BO_3 + 2NaCl$. Metaborates are also formed in the borax-bead reactions:

$$Na_2B_4O_7 + CuO = Cu(BO_2)_2 + 2NaBO_2.$$

Boron trioxide shows feebly basic as well as acidic properties. 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.

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 fractions ionised in 0·1

normal solutions at 18°: carbonic acid ($H{\cdot}HCO_3$), 0·0017; hydrogen sulphide ($H{\cdot}HS$), 0·0007; boric acid ($H{\cdot}H_2BO_3$), 0·0001.

It ionises as a monobasic acid and may be titrated with caustic soda after addition of a large amount 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 or sodium (Davy): $B_2O_3 + 6K = 2B + 3K_2O$; more conveniently by heating potassium borofluoride (*q.v.*) with potassium · $KBF_4 + 3K = 4KF + B$. The simplest 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, 1895)

EXPT 2.—Heat about 2 gm of a mixture of 5 gm. of magnesium powder with 15 gm. of powdered boron trioxide in a covered crucible When the violent reaction occurs, cool, and place the crucible in a beaker containing diluted hydrochloric acid (1 . 2). Filter and wash In the later stages of the washing, the boron may 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 said to be a solid solution of a **boron suboxide**, B_4O_3, or B_3O, 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, 1909) 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. 544): the nitride is prepared by heating borax with ammonium chloride, extracting with hydrochloric acid, and washing:

$$Na_2B_4O_7 + 2NH_4Cl = 2NaCl + 2BN + B_2O_3 + 4H_2O.$$

Boron burns when heated in nitric oxide: $5B + 3NO = B_2O_3 + 3BN$. 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 a **carbide**, 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 with carbon in the vapour of CS_2. The sulphide is hydrolysed by water: $B_2S_3 + 3H_2O = B_2O_3 + 3H_2S$. B_2S_5 is said by Moissan to be formed from BI_3 and S dissolved in CS_2. It would contain quinquevalent boron. **Metathioboric acid**, HBS_2, is formed in white needles by the action of H_2S on BBr_3

Crystalline boron was obtained by Deville and Wohler (1858) by fusing boron with aluminium at 1500° 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 diamond. Crystalline boron is very hard and 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 laminae of AlB_2 are also formed in Wohler's process.

Boron hydrides.–Equal weights of B_2O_3 and magnesium powder on heating form **magnesium boride**, which with acids evolves a gas with a peculiar smell, burning with a green-edged flame (F. Jones, 1879) Ramsay and Hatfield (1901) showed that the gas contains several hydrides, condensed by liquid air. BH_3 is not known.

The liquid condensed out of the gas from magnesium boride and hydrochloric acid by cooling in liquid air is a mixture of the hydrides B_4H_{10} (b pt 18°, m pt −119·7°), B_5H_9 (m. pt −46·9°), and B_9H_{10} (m. pt. −65·1°), separable by fractional distillation, B_4H_{10} being most volatile. At the ordinary temperature, these hydrides are colourless liquids Even pure B_4H_{10} rapidly decomposes at the ordinary temperature into hydrogen, diborane (B_2H_6, b. pt. −92·5°, m. pt. −165·5°), and many less volatile hydrides. B_2H_6 is very stable in the absence of moisture and grease; it reacts with water. $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$. On heating B_4H_{10} in a sealed glass tube at about 100°, B_2H_6, B_5H_9 and B_9H_{10} are formed. 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, or benzene A colourless solid, possibly $B_{12}H_{17}$, 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: $B_4H_{10} + 4KOH = 4KOBH_3 + H_2$. These decompose when acidified: $2HOBH_3 + 2H_2O = 2HBO_2 + 5H_2$. By the action of chlorine on B_2H_6, the compound B_2H_5Cl is obtained. (Stock, etc., 1912–24.)

Stock and Kuss (1923) by measuring the hydrogen evolved in the reaction: $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$ found the atomic weight of boron to be $10{\cdot}8055 \pm 0{\cdot}0015$.

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. $-107°$, b. pt. $12{\cdot}5°$, sp. gr. $1{\cdot}434$ at $0°$.

BBr_3, colourless, viscous liquid, m. pt. $-46°$, b pt. $90{\cdot}1°/740$ mm.

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**: $4BF_3 + 3H_2O \rightleftharpoons B(OH)_3 + 3HBF_4$. 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 is thrown down as an amorphous white precipitate on addition of a potassium salt to the acid. BF_3 readily combines with ammonia, giving a white solid, BF_3,NH_3. Borofluorides are formed in solution from boric acid and acid fluorides: $H_3BO_3 + 2NaHF_2 = NaBF_4 + NaOH + 2H_2O$. The acids $HClO_4$ and HBF_4 show similarities, especially in the capacity to form salts with organic bases.

Boron chloride, BCl_3, is obtained by burning amorphous boron in chlorine, by heating B_2O_3 with phosphorus pentachloride in a sealed tube at $150°$: $B_2O_3 + 3PCl_5 = 2BCl_3 + 3POCl_3$, 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.

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.

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."—Sodium "perborate," obtained by the action of hydrogen peroxide and caustic soda, or sodium peroxide, on cooled borax solution, formerly considered to be a perborate, $NaBO_3,4H_2O$, is not a true perborate but a borate containing hydrogen peroxide of crystallisation, $NaBO_2,3H_2O,H_2O_2$. It does not liberate iodine from concentrated potassium iodide solution. The compound ("perborax") is stable in the dry state and only sparingly soluble in water. The solution has bleaching and antiseptic properties and is also stable at room temperature but evolves oxygen on warming. The solid loses $3H_2O$ at 50°–55°, and if it is then heated in a vacuum at 120° it loses another molecule of water, leaving a yellow solid formulated as $(NaBO_2)_2O_2$, which evolves oxygen in contact with water, but does not liberate iodine from concentrated potassium iodide solution. The crystalline "perborate," $NaBO_2,H_2O_2,3H_2O$, is also obtained by the electrolysis of a solution of borax and sodium carbonate with a platinum gauze anode.

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 alkali, it turns greenish-black.

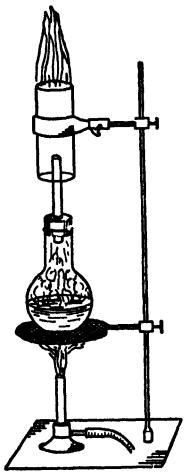


FIG. 335.—Green flame of ethyl borate.

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 3.—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. 335), 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 group separation of the metals, it is removed if its presence has been detected, by repeated evaporation of the solution with 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.

SILICON.

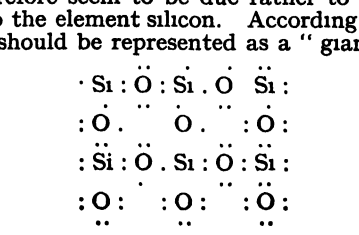
Silica.—Next to oxygen, silicon is the most abundant element in the crust of the earth: it occurs in combination with oxygen as **silicon dioxide**, or silica, SiO_2, varieties of which are quartz, sand, flint, etc. Silica is also the acidic constituent of the very abundant *silicate rocks*. Granite 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 1666. 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 1811 obtained **silicon** as a brown amorphous powder on passing the vapour of silicon fluoride over heated potassium, but its true character was not recognised 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, 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, difficulty-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. 76·74°; **silicon tetrachloride,** $SiCl_4$, b. pt. 56·8°.

Chloroform, $CHCl_3$, b. pt. 61·2°; **silicon chloroform,** $SiHCl_3$, b. pt. 33°.

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. According to G. N. Lewis the structure of silica should be represented as a "giant molecule":



The forms of silica.—Silica occurs both *crystallised* and *amorphous*. The three main crystalline forms are *quartz*, *tridymite* and *cristobalite*, although optically different forms of each exist, having definite transition points (Fenner, 1912–14):

$$\alpha\text{-quartz} \text{ (tetartohedral hexagonal)} \overset{575^\circ}{\rightleftharpoons} \beta\text{-quartz} \text{ (hemihedral hexagonal).}$$

$$\beta\text{-quartz} \overset{870^\circ \pm 10^\circ}{\rightleftharpoons} \beta\text{-tridymite} \text{ (holohedral hexagonal).}$$

$$\beta\text{-tridymite} \overset{1470^\circ \pm 10^\circ}{\rightleftharpoons} \beta\text{-cristobalite} \text{ (cubic).}$$

By rapidly cooling β-tridymite and β-cristobalite, they pass at the following temperatures into metastable forms with lower optical symmetry

$$\beta\text{-tridymite} \overset{163^\circ}{\rightleftharpoons} \beta_1\text{-tridymite} \overset{117\,4^\circ}{\rightleftharpoons} \alpha\text{-tridymite} \text{ (biaxial, perhaps orthorhombic).}$$

$$\beta\text{-cristobalite} \overset{198^\circ\text{-}275^\circ}{\rightleftharpoons} \alpha\text{-cristobalite} \text{ (biaxial).}$$

Silica occurs also in 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 deposits of almost pure silica are found 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*.

Quartz.—Quartz (sp. gr. 2·648) or *rock-crystal*, formerly believed to be "a hard form of ice," occurs sometimes in clear colourless crystals used for the preparation of spectacle lenses ("pebbles"), prisms, and optical apparatus, but more frequently 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.

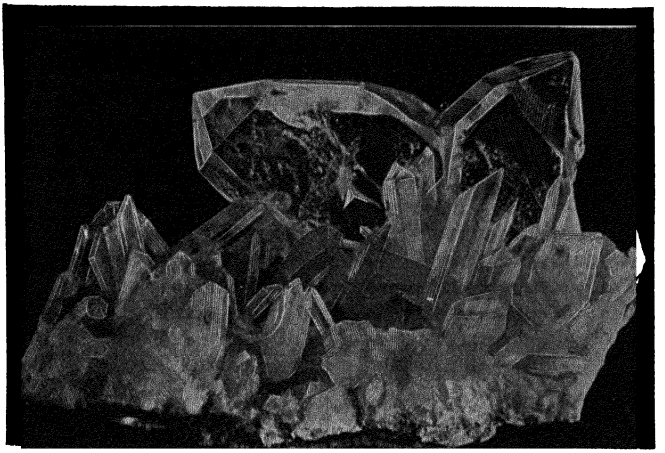


FIG. 336.—Crystals of quartz (British Museum).

"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 the crystal is really a tetartohedral trigonal trapezohedron, with lower symmetry, and possesses optical activity. Some crystals exhibit hemihedral facts inclined to the right, others to the left, so that one type of crystal is the mirror-image of the other (Fig. 337). Such pairs of crystals are known as **enantiomorphs**. 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 *dextrorotatory* quartz crystals rotate the plane of polarised light to the right, left-handed or *laevorotatory* crystals rotate it to the left. The rotation is proportional to the thickness of crystal traversed.

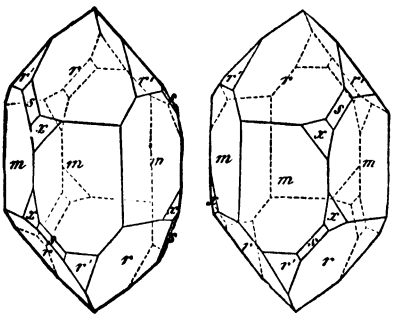


FIG. 337.—Enantiomorphous crystals of quartz.

Tridymite.—Tridymite (sp. gr. 2·31) occurs more rarely than quartz, in minute crystals, usually in the form of six-sided plates (Fig. 338) in cavities in the trachytic rocks of Mexico and Stenzelborg. It belongs to the hexagonal system.

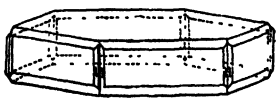


FIG. 338.—Crystalline form of tridymite

Quartz and tridymite appear to have been deposited from solution. If hydrated silica (p. 727) 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. Spezia (1905–9) obtained quartz crystals more than 1 cm long from solutions of quartz in sodium silicate and sodium chloride kept for some months at 330°

Cristobalite.—This tetragonal crystalline variety, discovered by Schwarz (1912), is obtained by heating powdered amorphous (fused) quartz at 1500°. It has a specific gravity of 2·32 to 2·41 and is very similar to tridymite. It is the stable form in high temperatures, and is found in some volcanic rocks and meteorites

Amorphous silica.—All the varieties of silica soften below 1600°, fuse in the oxyhydrogen blowpipe at about 1710°, and boil in the electric furnace at 2230°. They become plastic before fusion, and may be worked and blown like glass, or drawn into thread. The amorphous vitreous product, sp. gr. 2·2, called *quartz glass*, first made by Gaudin in 1839, has a very small coefficient of expansion (cubical coefficient $= 5 \times 10^{-7}$) and may therefore be heated to redness and quenched in cold water without fracture. Quartz crystals easily crack when heated. It is transparent to the ultra-violet rays, whilst ordinary glass is opaque. On heating quartz glass at about 1100°, it crystallises and becomes opaque: tridymite is formed. Hydrogen diffuses easily through heated silica glass, helium even at room temperature and very rapidly at 510°, and oxygen appreciably at 600°.

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, evolution of gas from which 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. **Chalcedony** is probably a fibrous variety of quartz; it is translucent

and yellow, sp. gr. 2·6, and the water present is probably absorptive only. Mixtures of amorphous silica with quartz or tridymite occur as the gems **carnelian** (red, due to ferric oxide), **sard** (brown-red), **chrysoprase** (apple-green, due to nickel), **onyx** and **sardonyx** (red). Common **flint** occurs in rounded nodules in chalk ("chert"), coloured yellow, grey or black by oxide of iron and organic matter. 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. *Waxy opal* is found in large quantities in Queensland *Tabaschir* is a porous variety of opal found inside bamboo canes. Gelatinous silica was found in excavating for the Simplon Tunnel

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 may indicate that they have been deposited in layers from water on the sides of a "pipe," or, as is now thought, may be due to diffusion through a gel. *Liesegang rings* similar in structure, are formed when a drop of silver nitrate solution is placed on a gelatine jelly containing a little potassium dichromate. The **cat's eye** consists of crystals of quartz enclosing fibres of asbestos. **Jasper** is opal deposited in layers of various colours.

Amorphous silica may be obtained from silicates by fusing the finely-powdered mineral with excess of potassium and sodium carbonates in a platinum crucible until evolution of carbon dioxide ceases. Alkali silicates are formed: $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$. 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, when the silica becomes granular and quite insoluble in water. It is washed with boiling hydrochloric acid until 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. If the mineral contains titanium, the silica will contain titanium dioxide. A qualitative test is to heat a fragment of the mineral in a microcosmic salt bead (p 625): metallic oxides dissolve, and a skeleton of silica is left floating in the bead. A sodium carbonate bead dissolves silica with effervescence, and remains clear on cooling.

At high temperatures silica, being practically non-volatile, displaces volatile acids from their salts: $Na_2SO_4 + SiO_2 = Na_2SiO_3 + SO_3$. 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 alkali silicates, is appreciably soluble in water, alkalies, sodium carbonate and acids.

If a dilute solution of sodium silicate is poured slowly, with stirring, into an excess of dilute hydrochloric acid, no precipitation 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 the sodium and chloride ions diffuse out, leaving a clear **colloidal solution** or **hydrosol** of **silicic acid** 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, **silica hydrogel** 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.

When silica gel is dried in the air, it retains about 16 per cent. of water. At 100°, 13 per cent. of water remains, and the silica is then insoluble. On further heating, water is gradually lost; according to van Bemmelen the vapour-pressure curve shows no breaks indicative of hydrates but Tammann considers that it exhibits definite breaks corresponding with **orthosilicic acid**, H_4SiO_4, and **metasilicic acid**, H_2SiO_3. Maschke (1872) noticed that the clear gel becomes white and opaque when a certain amount of water is removed but becomes clear again on further drying. 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. After heating at 300° the gel contains about 4 per cent. of water; it is only after prolonged heating at 900°–1000° that all the water is lost. The hydrated form of silica precipitated when silicon fluoride or chloride is decomposed by water has the composition of orthosilicic acid, $Si(OH)_4$, when washed rapidly with benzene and ether and dried between filter-paper at the atmospheric temperature.

Although the existence of definite silicic acids was assumed by many chemists, the work of van Bemmelen gave rise to the impression that they were all colloidal associations of water with silica. Tammann

showed, as stated above, that van Bemmelen's results really indicated the existence of silicic acids, and more recent work has confirmed this.

Organic derivatives of silicic acids are quite definite compounds. Esters of silicic acids were first investigated by Wurtz in 1863. Ethyl and methyl orthosilicates, $(C_2H_5)_4SiO_4$ and $(CH_3)_4SiO_4$ are liquids boiling at 60°–62° and 25°, respectively, under 12 mm pressure They are obtained by the action of $SiCl_4$ on the anhydrous alcohols Methyl silico-orthoformate, $SiH(OCH_3)_3$, b. pt. 104°–6° at 760 mm., is obtained from methyl alcohol and $SiHCl_3$. Ethyl metasilicate, $SiO(OC_2H_5)_2$, b. pt. 233°, is obtained from $SiCl_4$, ethyl alcohol and a little water. By heating quartz powder with sodium carbonate in the required proportions at 1150°, sodium metasilicate, disilicate and trisilicate are formed, from which, according to Tschermak, the free acids, H_2SiO_3, $H_2Si_2O_5$ and $H_4Si_3O_8$, are formed as granular white powders by treatment with 80 per cent. sulphuric acid at 10°. As so obtained the acids contain 5 per cent. excess of water, which may be removed by treatment with alcohol and ether Orthosilicic acid cannot be obtained by this method but is formed by the slow hydrolysis of ethyl orthosilicate · $(C_2H_5)_4SiO_4 + 4H_2O = H_4SiO_4 + 4C_2H_5OH$. By loss of water it gives the acids $H_2Si_2O_5$ and H_2SiO_3.

According to Tschermak, the composition of a silicate may be ascertained by treatment with concentrated hydrochloric acid, when the corresponding silicic acid is set free.

The existence of definite potassium silicates . K_2SiO_3, m pt 976°, $K_2Si_2O_5$, m pt 1036°, and $K_2Si_4O_{13}$, m pt 765°, has been proved from the freezing point curves, and many others will no doubt be discovered in due course.

The silicates.—Although silicon does not form such a large number of compounds as carbon, the silicates enter into the composition of an extensive series of *rock-forming minerals*, the formulae of which are often rather complex. Many silicates, however, may be regarded as salts of silicic acids, *e.g.*, 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.**

As indicated by X-ray analysis, the structures of quartz and of many silicates may be almost entirely determined by the packing of oxygen atoms (or ions, O'') in the crystals, the other atoms being (with the exception of sodium, calcium and potassium ions) relatively much smaller than the oxygen atoms and fitting into the interstices between the close packing of the latter. This close packing is, however, not general, since many silicates have more complex structures. Close

packings of three and of four oxygen atoms to form tetrahedral and octahedral arrangements, respectively, are supposed to be built up into crystal structures, giving cubic and hexagonal pyramid structures, respectively. The small silicon and aluminium ions with large positive charges, Si^{4+} and Al^{3+}, fit in between the negative oxygen ions and exert large electrical forces, making the resulting structure very hard.

Orthorhombic olivine, $(Mg,Fe)_2SiO_4$, contains the separate ion SiO_4^{4-} of orthosilicates. Each magnesium atom is surrounded by six oxygen atoms somewhat distorted from the ideal octahedral arrangement. The structure of some silicates is more open, as in the arrangement in beryl, $Be_3Al_2Si_6O_{18}$, in which every silicon atom is surrounded by four oxygen atoms arranged tetrahedrally, every aluminium by six oxygen atoms at the corners of an octahedron, and every beryllium atom by four oxygen atoms at the corner of a distorted tetrahedron. Six silicon tetrahedra are linked by corners into a hexagonal ring, of composition Si_6O_{18}. These rings are linked by beryllium between four oxygen atoms, and aluminium between six oxygen atoms. There are wide open channels in the structure where the Si_6O_{18} rings surround the hexagonal axis. The silicon is at the centre of four oxygen atoms and the three to one ratio is brought about by each silicon tetrahedron sharing two of its corners with neighbouring silicon tetrahedra

Silicon.—Silicon has a great affinity for oxygen : $[Si]+(O_2)=[SiO_2]$ $+191$ k. cal., so that the direct reduction of silica can be effected only by the use of powerful reducing agents or at high temperatures, as when silica is heated with carbon in the electric furnace : SiO_2+2C $=2CO+Si$. Silicon is made in this way at Niagara by heating a mixture of sand and crushed coke, or by reducing silica with calcium carbide. It is a hard grey crystalline mass, with the appearance and electric conductivity of graphite, m. pt. 1414°, b pt. 2392°. Silicon 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 (*ironac, tantiron, narki*, etc.) is very resistant to the action of acids, except hydrochloric, which requires 50 per cent. of silicon.

In the laboratory, silicon is most conveniently prepared by heating silica with magnesium powder : $SiO_2+2Mg=2MgO+Si$.

EXPT. 4.—Two grams of a mixture of 5 parts of powdered quartz or *thoroughly dried* amorphous silica with 3 parts of magnesium powder and 2 parts of calcined magnesia to moderate the reaction, are 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

Amorphous silicon so prepared is a light 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 a mixture of nitric and 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, or in fused sodium carbonate, potassium nitrate or potassium chlorate: $Si + 2KOH + H_2O = K_2SiO_3 + 2H_2$.

Amorphous silicon when strongly heated in a closed crucible 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 sodium and zinc, or with 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 of **adamantine silicon**; aluminium gives six-sided plates of graphitoidal silicon; both varieties are made up of regular octahedra. Crystalline silicon has a density of 2·39; it does not burn in oxygen even when strongly heated, but burns when heated in chlorine, and ignites spontaneously 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: when fused with sodium carbonate it displaces carbon: $Si + Na_2CO_3 = Na_2SiO_3 + C$. Another variety (sp. gr. 2·42), formed on crystallising from molten silver, is soluble in hydrofluoric acid.

Silicon hydrides.—Silicon and hydrogen combine to some extent at the temperature of the electric arc, forming silicon hydride, SiH_4, **silicon-methane**, or **monosilane**: $Si + 2H_2 \rightleftharpoons SiH_4$. If magnesium powder and *dry* 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 bluish crystalline mass This, when treated with dilute hydrochloric acid in a flask from which air has been displaced by hydrogen, evolves a spontaneously inflammable gaseous mixture of silicon hydrides with hydrogen: $Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$ (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.* phosphine).

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 liquid mixture of hydrides of silicon is condensed, from which, by fractionation, the following compounds may be isolated:

1. **Monosilane**, SiH_4, m. pt. $-185°$, b. pt. $-112°$, is a colourless gas, stable at the ordinary temperature, spontaneously inflammable if mixed with the other hydrides and sometimes if pure; relative density 16·02, 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, 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, $NaOC_2H_5$:

$$SiHCl_3 + 3C_2H_5ONa = SiH(OC_2H_5)_3 + 3NaCl.$$

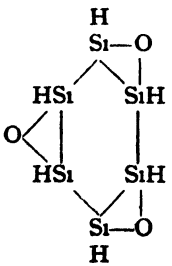
2. **Disilane**, Si_2H_6 (**silicon-ethane**), also prepared by the action of concentrated hydrochloric acid on lithium silicide. $Li_6Si_2 + 6HCl = 6LiCl + Si_2H_6$, is a colourless gas, b. pt. $-15°$, m. pt. $-132·5°$, stable at the ordinary temperature, but rapidly decomposed at 300°, relative density 3I·7, inflames in the air; soluble in benzene and carbon disulphide, and 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 yellow solid obtained by the action of dilute hydrochloric acid on calcium silicide has been stated to be silicon acetylene, Si_2H_2, or silicone, $(HSi)_2O_2$, or oxydisilin, $Si_2H{\cdot}OH$. By the action of dilute alcoholic hydrogen chloride on $CaSi_2$, Kautszky (1921–23) obtained a white crystalline compound, **siloxene**:



Siloxene inflames spontaneously in air and decomposes water. By the action of bromine on siloxene under CS_2, a yellow **silical bromide**, $Si_6O_3H_3Br_3$ is formed, which is hydrolysed by water into a brownish-red **silical hydroxide**, $Si_6O_3H_5OH$, a base giving coloured salts.

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 with all the halogens of the types SiX_4 and $SiHX_3$, are known; isolated compounds of the types SiH_2X_2 and SiH_3X have been prepared, and a number of chlorides not corresponding with the type SiX_4 are also known.

Silicon tetrachloride (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: $SiCl_4 \leftarrow 2Cl_2 + Si\,O_2 + 2C \rightarrow 2CO$. The products of reaction are cooled in a worm-tube, when silicon tetrachloride condenses as a colourless volatile liquid, sp gr. $1·50$ at $0°$, m. pt. $-70°$, b. pt. $56·8°$, 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, $SiCl_4,6NH_3$, and its vapour forms dense fumes with ammonia.

By the action of chlorine on silicon, besides $SiCl_4$, two other chlorides are formed the **trichloride**, Si_2Cl_6 (m. pt. $-1°$, b. pt. $145°$), and the **octachloride**, Si_3Cl_8 (b. pt. $210°$–$215°$). These may be separated by fractionation The trichloride is also produced when the vapour of the tetrachloride is passed over strongly-heated silicon. It is a colourless fuming liquid, the hot vapour of which ignites spontaneously in the air With water, it produces an explosive white solid, $Si_2H_2O_4$, or $(SiO\,OH)_2$, **silicon-oxalic acid**: $Si_2Cl_6 + 4H_2O = (SiO_2H)_2 + 6HCl$. The octachloride forms with water a white powder, $H_2Si_3O_5$, **silicon-meso-oxalic acid**, the structural formula of which has been given as $SiO_2H.SiO.SiO_2H$. The compounds Si_4Cl_{10}, Si_5Cl_{12} and Si_6Cl_{14} have been described

According to Troost and Hautefeuille, Si_2Cl_6 vapour begins to decompose at $350°$, and is completely dissociated at $800°$: $2Si_2Cl_6 \rightleftharpoons 3SiCl_4 + Si$. At high temperatures ($1000°$) reaction begins in the reverse direction, and the vapour is stable.

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. Si_3Br_8 and Si_4Br_{10} are formed by the action of the silent discharge on silicon-bromoform, $SiHBr_3$.

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

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 440°) are stated to be formed, separable by fractionation

Silicon chloroform, $SiHCl_3$, b. pt. 33°, m. pt. −134°, sp. gr. 1·3438, discovered by Buff and Wohler, is prepared by passing hydrogen chloride over silicon (or the mixture of silicon and magnesia, p. 733) 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. 56·8°) 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 into Si, H_2, HCl, $SiCl_4$, and a trace of less volatile liquid.

By the action of ice-cold water on silicon chloroform, **silicoformic anhydride** $H_2Si_2O_3$, a white solid, probably polymerised $[SiH(O)]_2O$, is formed. This is a powerful reducing agent: $H_2Si_2O_3 + O_2 = 2SiO_2 + H_2O$ (*cf* formic acid $H\,CO_2H + O = CO_2 + H_2O$). 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 −100°), is produced 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.*, $SiCl_3Br$, have been described

Silicon fluoride.—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, some dehydrating agent is added. Usually a mixture of powdered fluorspar and white sand in equal proportions is heated in a thick 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 4·684 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 941 mm. pressure Ammonia solution decomposes the gas with separation of gelatinous silica : $SiF_4 + 4NH_4OH = H_4SiO_4 + 4NH_4F$.

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 $SiHF_3$, **silicon fluoroform,** analogous to silicon chloroform, is obtained from this by the action of stannic fluoride or titanium tetrafluoride, and is a combustible gas, b. pt $-80·2°$, m pt $-110°$, which decomposes on heating $4SiHF_3 = 3SiF_4 + 2H_2 + Si$, and in contact with water . $2SiHF_3 + 4H_2O = H_4SiO_4 + H_2SiF_6 + 2H_2$

Hydrofluosilicic, or silicofluoric, acid.—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 soluble acid, H_2SiF_6, called hydrofluosilicic acid or silicofluoric acid : $3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6$. 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 : $H_4SiO_4 + 6HF = H_2SiF_6 + 4H_2O$. The acid is prepared on the large scale (for lead refining, *q v*) by percolating aqueous hydrofluoric acid through sand.

EXPT 5.—Heat a mixture of 50 gm. of powdered fluorspar, 50 gm of fine white sand, and 200 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 a cylinder, the gas delivery tube dipping under an inch of mercury at the bottom over which water is afterwards poured This is to prevent the tube becoming choked by the gelatinous silica (Fig. 339). 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).

A *concentrated* solution of hydrofluosilicic acid fumes in the air. The anhydrous acid is not known, but 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:

$$H_2SiF_6 + 2NaOH = Na_2SiF_6\ (pp) + 2H_2O;$$
$$Na_2SiF_6 + 4NaOH = 6NaF + H_4SiO_4\ (pp.).$$

The end-point, with phenolphthalein, is therefore reached when *six* molecules of base have been added per molecule of acid.

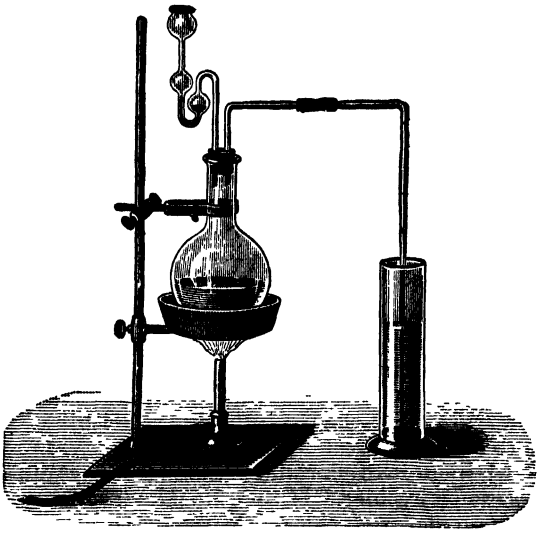


FIG 339.—Preparation of Hydrofluosilicic acid

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. 603).

Salts of hydrofluosilicic acid are called **silicofluorides**, or **fluosilicates**; they are prepared 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: K_2SiF_6, Na_2SiF_6, $BaSiF_6$, $CaSiF_6$, rare earths. The salts K_2SiF_6 and Na_2SiF_6 are formed as nearly transparent gelatinous precipitates; $BaSiF_6$ forms a white crystalline precipitate; strontium salts are not precipitated. The lithium salt, Li_2SiF_6, is

soluble in water, and the solution precipitates Na_2SiF_6 with sodium chloride.

Silicon carbide.—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), 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 diamond. The technical product, *carborundum*, is a black, coarsely-crystallised mass exhibiting a play of iridescent colours It is very difficultly fusible and may be used in furnace-linings, it 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 silicon carbide forms transparent, colourless or green, six-sided plates, sp. gr. 3·1, and is obtained by fusing silicon with carbon in the electric furnace.

Carborundum has the same lattice as diamond in which half the carbon atoms are replaced by silicon The carborundum in the electric furnace is 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 with sulphur, it is instantly decomposed by water into hydrogen sulphide and gelatinous silica It is also formed by passing the vapour of carbon disulphide over a strongly-heated mixture of silica and carbon: $SiO_2 + CS_2 + C = SiS_2 + 2CO$.

CHAPTER XXXVII

SPECTRUM ANALYSIS

The spectrum.—A solid or liquid, heated to a sufficiently high temperature, becomes luminous. At very high temperatures, the light emitted is white (*e.g.*, the limelight, p. 154). Such white light, or sunlight, when passed through a glass prism is broken up into a series of coloured rays called a spectrum. The rays of different colours are bent or refracted by the prism to different extents, the red rays the least, whilst the violet rays suffer the largest deviation. The spectrum 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 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 of quinine salts and some other substances. These are the **ultra-violet rays.**

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 electromagnetic waves which 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; X-rays and the γ-rays from radium are very short. Wave-lengths of radiation are usually measured in tenth metres, *i.e.*, 10^{-10} m., or **Ångström units** (A.U.). The μ and mμ units (p. 5) may also be used.

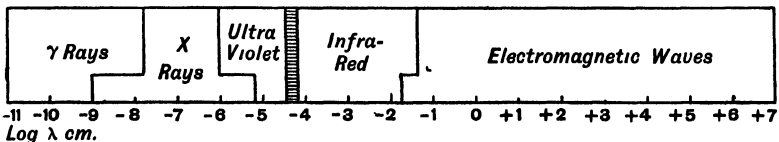


FIG 340

The above diagram and table (in A.U.) give the wave-lengths (λ) of all parts of the spectrum so far investigated. The numbers range from 0·1 to 10^{14} A.U.; the visible spectrum extends only over the very

restricted range of 4000 to 7000 A.U. The gap between the ultra-violet and X-rays is bridged by short radiations in the hydrogen spectrum (Lyman).

Electric 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 -	200 to 3970
Yellow - -	5750 to 5850	X- and γ-rays	500 to 0 1
Green - -	4920 to 5750		

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 wire. With increasing temperature the visible spectrum extends gradually towards the violet, and when a dazzling white light is emitted a continuous spectrum is obtained.

Small quantities of various salts, such as sodium, potassium, lithium, thallium and strontium chlorides, heated on platinum wires in a non-luminous Bunsen flame, impart characteristic colours to the flame

sodium salts yellow	thallium salts green
potassium salts lilac	strontium chloride red
lithium salts . crimson	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 separate lines, each corresponding with a definite wave-length, *i.e*, they are **line spectra**; 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; the spectrum of every element is characteristic, and serves for its identification. This is the principle of **spectrum analysis**, introduced into chemistry by Bunsen and Kirchhoff in 1859.

The visible spectra of salts usually correspond with those of the metals contained in them; that of sodium chloride, for example, is identical with the spectrum of metallic sodium. The salt vapours at the high temperature of the flame are dissociated 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.

The spectra of molecules differ in appearance from those of atoms. Instead of sharp lines, they consist of broad luminous

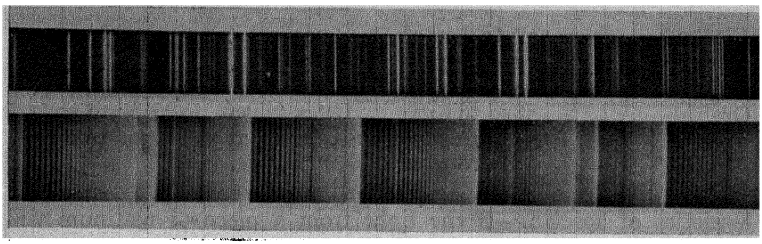


FIG. 341—Line and band spectra of nitrogen.
(*By courtesy of Prof. A. Fowler.*)

bands, often with a fluted appearance (Fig. 341), 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, which crowd together at the sharp edge of the band.

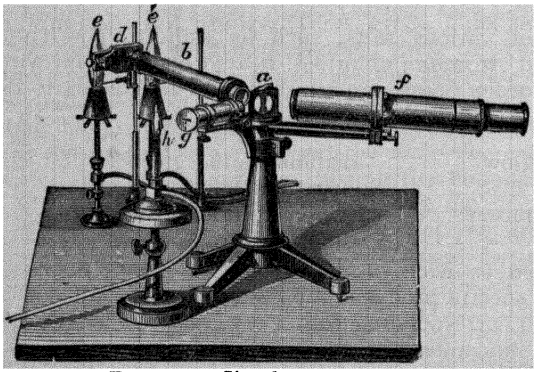


FIG. 342.—Simple spectroscope.

The spectroscope. —A convenient instrument for examining spectra is the spectroscope, invented by Bunsen and Kirchhoff, shown in Fig. 342.

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. 343. 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

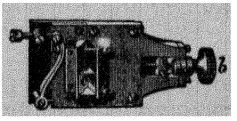


FIG. 343.—Adjustable slit of spectroscope.

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, it is compared with the positions of lines given by standard elements on a **wave length curve** plotted for the scale readings of the instrument.

A convenient small form of spectroscope for qualitative work is the **direct vision** instrument (Fig 344), in which the spectrum produced by

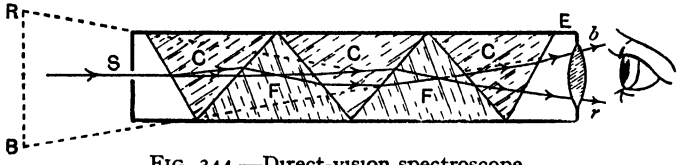


FIG 344 —Direct-vision spectroscope

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*.

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. 87). 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. 345, one or two Leyden jars being put in parallel with the coil. 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.

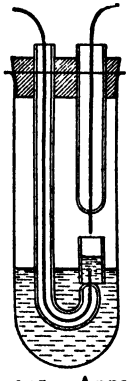


FIG 345 —Apparatus for producing spark spectra

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 thermopile or 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^{-6} 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. 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 without gelatin is used For still shorter waves (X-rays), ordinary plates are again used

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 Plucker 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 Every atom (except hydrogen) has several characteristic spectra according to the method of production (spark spectrum, arc spectrum). Variations of pressure in gases lead to broadening and even to slight displacements of spectrum lines (Humphreys and Mohler, 1895), and slight differences exist in the positions of lines in the iron spectrum as given by the sun and by the iron arc. 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.

The spectroscope is capable of revealing the presence of very minute quantities of certain elements—far below the possibility of detection by chemical analysis A quantity of $\frac{1}{1000000}$ mgm. of sodium may be detected, and all ordinary 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 practically be 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, carefully mapped by Fraunhofer in 1814, who found that they always occurred in the same positions in the spectrum, 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 first clearly stated by Kirchhoff in 1860, who repeated an experiment made by Foucault in 1848. 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, which 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 transparent to other rays. If the intensity of the light passing through the flame is greater than that of the light emitted by the flame, the absorption 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 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 it

Expt. 1 —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 (Fig 346). A small Bunsen burner with a bead 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.

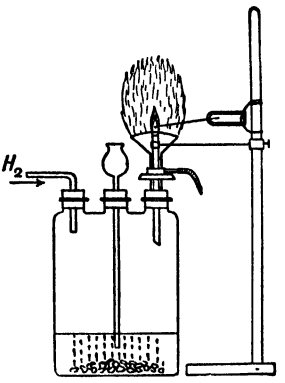


Fig 346 —Reversal of sodium line in spectrum

The presence of sodium vapour in the atmosphere of the sun may be inferred from the *dark* lines in the spectrum. The *bright* parts of the spectrum teach us nothing, because they are merely parts of the continuous spectrum emitted by *any* solid body raised to incandescence, and a sufficiently thick layer of incandescent gas will emit a continuous spectrum; this probably corresponds with the constitution of the sun. The *dark* lines of the spectrum, corresponding with absorption in the solar atmosphere, indicate the presence of corresponding elements in the sun. Certain stars and nebulae, 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 laboratory bench.

Absorption spectra.—If white light is transmitted through a transparent coloured body, such as ruby glass or a solution of indigo, the emergent light when 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 various parts of the spectrum.

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.

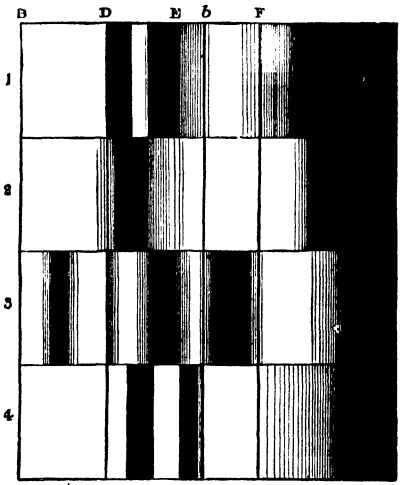


FIG. 347.—Absorption spectra of blood.

The absorption spectra of blood are shown in Fig. 347. No. 1 shows two dark bands, D and E, due to oxyhaemoglobin, given by oxidised blood. No. 2 shows the absorption spectrum of de-oxidised blood, in which there is only one dark band, due to haemoglobin. By the action of acids on blood, the haemoglobin is converted into haematin, the oxidised and de-oxidised forms of which give the spectra Nos. 3 and 4. Carbon monoxide, nitric oxide and hydrocyanic acid from compounds with haemoglobin giving characteristic absorption spectra.

CHAPTER XXXVIII

METALS AND ALLOYS

Metals.—The name *metal* is derived from the Greek μέταλλον, first used by Herodotos (450 B C) in the sense of a *mine*. Gold, silver, copper, iron, tin and lead were known to the ancient Egyptians and Babylonians they are mentioned in the Old Testament and by early Greek authors. Mercury is mentioned by Aristotle (384–322 B C). Zinc is referred to by Strabo (10 A.D.) and bismuth by Agricola (1530 A D) Antimony was known in Egypt and Babylonia; its compounds are carefully described by "Basil Valentine" (p. 27) 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. Only a few metals, 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. 404) The principal methods used for the **extraction of metals** may be briefly summarised.

Native copper, gold and the platinum metals are worked up by refining. Other industrial processes for the extraction of metals include (small scale extractions in brackets)

(1) reduction of the oxides with hydrogen · tungsten, (all metals with atomic weights greater than that of manganese),

(2) reduction of oxides with carbon. zinc, cadmium, aluminium (electrolytic), tin, bismuth, manganese, iron, cobalt, nickel; titanium, zirconium, thorium in electric furnace; many special steels by simultaneous reduction of the oxide with carbon and iron, (metals after group III, some at high temperature in electric furnace);

(3) reduction of oxides with aluminium (*thermit process*) chromium, manganese; (on the small scale magnesium, or mischmetall, p. 891, may replace Al),

(4) oxidation of sulphides, either directly by atmospheric oxygen, as with mercury ($HgS + O_2 = Hg + SO_2$), or by partial oxidation and interaction of sulphide with oxide or sulphate, as with copper (p 786) and lead (p 903),

(5) reduction of sulphides with iron antimony, tungsten,

(6) electrolytic processes electrolysis of (*a*) fused hydroxide, for sodium (potassium, etc), (*b*) fused chloride for magnesium and calcium (strontium, etc), (*c*) solutions of salts, for copper, silver, nickel, chromium, (with mercury cathode for several metals, followed by heating amalgam),

(7) special processes, carbonyl process for nickel (p. 986)

Alloys.—Two or more metals when fused together usually, but not always (*e g*, zinc and lead, p. 801), form a homogeneous liquid, and the intimate association of the metals formed on solidification is called an alloy. The name, used in this sense by Chaucer, is derived from the Latin *alligare*, Mediaeval Latin, *alloiare*, "to bind to." Although the preparation of alloys by fusion is the method 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.*, tungsten and iron compounds in the electric furnace), are alternative processes. Alloys containing mercury are called **amalgams**, a word which may have been derived from Arabic *al magma* (Greek, *magma*), a mixture.

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 be present in alloys; hard steel, prepared by quenching, is a solid solution of iron carbide, Fe_3C, in a particular allotropic form of iron (γ-iron).

If the solid alloy is heterogeneous, the separate phases may consist of. (i) *pure metals*; (ii) one or more *pure compounds*; or (iii) *solutions* of metals or their 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 metals forming a **binary alloy**, and shall suppose that this alloy is either a heterogeneous mixture of the two pure components, or else consists of one or more chemical compounds, with or without an excess of one of the pure components. The consideration of solid solutions is omitted.

Consider first the case in which no chemical compounds are present. If pure silver is fused and allowed to cool, it begins to solidify (if supercooling is absent) at the freezing point, 960·5°, represented on the diagram (Fig 348) by the point *A*. In the diagram temperature 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 alloy. Thus, the end *P* of the line corresponds with 0 part of the second metal, say copper, and the point *A* on the vertical line above *P* represents the melting point of pure silver (atoms of copper = 0; atoms of silver = 100) The point *Q* represents pure copper (atoms of copper = 100, atoms of silver = 0), and *B* is the melting point of pure copper, 1083° A point midway on the line *PQ* represents a mixture of equiatomic amounts of copper and silver The proportions of copper in the alloys are represented on the upper scale, those of silver on the lower scale; the sum is always 100

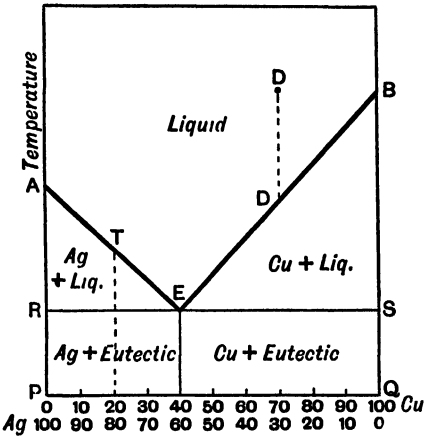


FIG 348 —Freezing point curves of binary alloy forming eutectic

If a little copper is added to the silver, the fused alloy begins to solidify at a temperature slightly lower than the melting point of pure silver, since a dissolved substance lowers the freezing point of silver, provided pure silver separates on cooling (p 86). This temperature will be represented by a point a little to the right of *A*, and somewhat lower. By adding successive amounts of copper, the freezing points become progressively lower and lie on the curve *AE*. If the molecular depression of freezing point were constant, this would be a straight line, which has been drawn in Fig 348 for simplicity, usually *AE* is not straight, since the laws of dilute solutions do not apply strictly. The depression of freezing point continues as more copper is added, until at a certain point, *E*, both silver and copper begin to separate side by side This is the **eutectic point** (p 86), 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 (40 : 60 in the diagram) will solidify completely at the eutectic temperature.

Exactly the same conditions apply to the addition of silver to copper. In this case the freezing points of various alloys lie on the curve *BE*, running down from the freezing point, *B*, of pure copper. The eutectic point *E* is again reached, when silver begins to separate along with the copper.

At all points above *AEB* 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. In the region *BSE* pure copper separates. At the eutectic temperature, represented by *RS*, both metals 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 copper, this metal will begin to separate in the solid state. The still liquid part will become richer in silver, and will then freeze at a somewhat lower temperature. Both the composition and freezing point will now be represented by a point on the curve nearer to *E*. As solidification proceeds, the temperature falls until finally the eutectic point *E* is reached, when silver begins to separate along with the copper, and the whole mass then solidifies at the eutectic temperature.

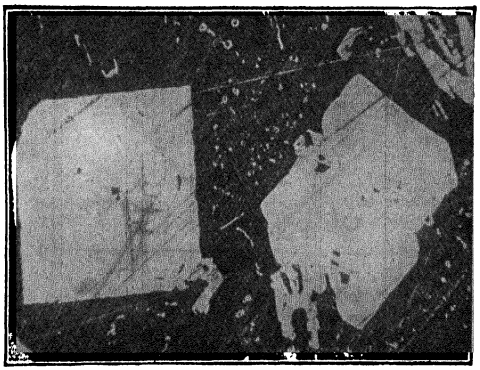


FIG. 349.—Microscopic appearance of solidified alloy

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, crystals of one metal, which separated along *D'E*, embedded in a matrix of eutectic alloy are seen. The latter is always composed of small crystals. (Fig. 349).

In the second place consider an alloy in which metallic compounds are formed, say tin and magnesium, which form Mg_2Sn. The freezing-point curve is shown in Fig. 350.

The compound Mg_2Sn has a definite melting point, 783·4°, represented by *C*. If pure tin is added to the fused compound, or to a mixture of the metals in the requisite proportions, the freezing point is lowered. The solid separating along CE_1 is pure Mg_2Sn. Finally a eutectic point E_1 is reached, at which Mg_2Sn and Sn separate together. If magnesium

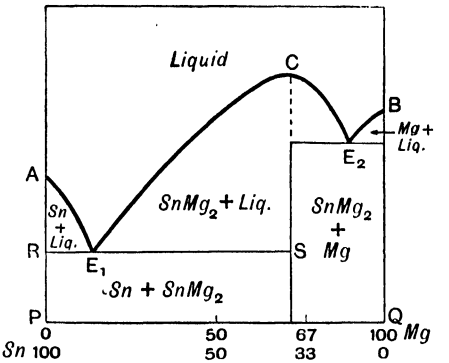


Fig. 350.—Freezing-point curves of binary alloy forming one compound.

is added to pure tin, the freezing point of the latter is depressed along AE_1, the solid separating being pure tin until E_1 is reached, when tin and Mg_2Sn separate. The solid alloy obtained on cooling a liquid mixture of composition C will be homogeneous Mg_2Sn. 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 crystals of Mg_2Sn embedded in a matrix of a eutectic mixture of Mg_2Sn and Sn.

Exactly similar relations hold for the addition of an excess of magnesium to Mg_2Sn, or tin to excess of magnesium, when a second eutectic point E_2 will appear Between E_2 and B pure magnesium separates, at E_2 the eutectic Mg_2Sn with magnesium separates

If we commence with pure tin and add increasing amounts of magnesium, the freezing points will make up the 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 partly dissociated in the liquid state $Mg_2Sn \rightleftharpoons 2Mg + Sn$ 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

The metallic state.—Maxwell, the originator of the electromagnetic theory of light, recognised that the opacity of metals is connected with their good conducting power for electricity, and Lorentz was able to account for their electrical and thermal conductivities by assuming that metals consisted of free mobile electrons, behaving like gas atoms, together with massive positive metal ions The electric current through a metal is carried entirely by the free electrons The difficulty of this theory was the fact that the electrons appear to contribute nothing to the heat energy of the metal, whereas if they behaved like free gas atoms, each should possess the kinetic energy of an atom of a monatomic gas Various modifications of the theory were proposed to account for the discrepancy Sommerfeld (1928) showed that the existence of free electrons in metals, which is made very probable by the phenomenon of **thermionic emission**, or the ejection of electrons from heated metals (utilised in wireless valves), can be made compatible with the specific heats by means of the new quantum theory of gases due to Fermi (1926) The " electron gas " is then found, on account of the extremely small mass of the electrons, to be in the same thermal state at temperatures up to 1000° as ordinary massive atoms at very low temperatures, when the quantum distribution allows the latter to have only small energies (see p. 385). It follows that the electrons in a metal have practically no heat energy Fermi's theory is remarkable in that it assumes a quantisation of *translational* energy, which is sometimes regarded as speculative In a corresponding theory due to Einstein and Bose, light and radiation are treated as " photon gas," and Planck's radiation formula then follows on statistical grounds.

CHAPTER XXXIX

THE ALKALI METALS

The alkali-metals.—Under the name **alkalies** are included the hydroxides, MOH, of the metals **lithium, sodium, potassium, rubidium** and **caesium.** The radical **ammonium,** NH_4, although it has not been isolated, behaves in its compounds as a univalent alkali-metal and forms an amalgam with mercury, 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.	Caesium
Atomic number	3	11	19	37	55
Electron configuration	2·1	2·8·1	2 8·8·1	2·8·18 ·8·1	2·8·18 ·18·8·1
Density at 0°	0·59	0 9723	0 859	1·525	1 903
Atomic volume	11·8	23·7	45·5	56 1	69·8
Melting point	186°	97·9°	62·04°	39·0°	28·45°
Boiling point	1609°	882 9°	762°	700°	670°
Colour of vapour	?	purple, green fluorescence	green	blue	?
Decomposing action on water	slow	rapid, hydrogen does not burn	rapid, hydrogen burns	rapid, hydrogen burns	rapid, hydrogen burns
Oxides	Li_2O, Li_2O_2,	Na_2O, Na_2O_2, Na_2O_3,	K_2O, K_2O_2, K_2O_3, K_2O_4,	Rb_2O, Rb_2O_2, Rb_2O_3, Rb_2O_4,	Cs_2O, Cs_2O_2, Cs_2O_3, Cs_2O_4,

The gradation in properties with increasing atomic number is clear. The metals of the alkalies are the most electropositive elements known; they never produce acids or complex anions, and they displace all other metals from their salts. In the group itself, the electropositive character increases from lithium to caesium, the latter being the most electropositive metal. The basicity of the hydroxides increases in the same order.

The alkali-metals are univalent, forming salts of the type MX; although many higher halogen compounds are known, these contain polyvalent halogen: examples recently investigated are RbI_3, CsI_3, CsI_4, $CsBr_3$, CsI_2Br, $RbClBrI$, $KICl_2$, $KICl_4$, $CsIBr_2$, $CsFICl_3$, $RbFICl_3$. CsI_9, RbI_7 and RbI_9 have been described. Some exist only in combination with solvent, *e g*, $LiICl_4, 4H_2O$, KI_3, H_2O; KI_7, H_2O.

The alkali-metals all combine directly on heating with hydrogen, forming solid, non-metallic, salt-like **hydrides**, MH, decomposed by water $MH + H_2O = MOH + H_2$.

The vapour densities of potassium and sodium correspond approximately 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 in the class of acids common *vinegar* or crude **acetic acid**, produced by the oxidation of wine or beer, which become sour on exposure to air (Greek *oxos*, vinegar, *oxus*, sour), also sour fruit juices and sour milk 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 The **mineral acids** (sulphuric, nitric, hydrochloric) were discovered by the alchemists Scheele (1770–1786) isolated a number of **organic 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 react 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 is a true acid, though a weak one.

(6) Cavendish (1766) showed that hydrogen is evolved by the action of acids (except nitric) on zinc, iron and tin.

Examples of **alkaline substances**, viz., slaked lime, plant and 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. Pliny mentions the *causticization* of alkalies by boiling with quicklime as known in Egypt. The Iatrochemists first described the general properties of alkalies Later, 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, and the names **mild alkali** and **caustic alkali** were introduced for the alkali before, and after, treatment with quicklime.

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 , dilute acids usually feel very harsh)

(2) They restore the blue colour of dyes reddened by acids (*e g.*, red cabbage, litmus), and turn 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 known to Duhamel in 1736. Marggraf (1757) differentiated between potash and soda as follows :

	Potash.	**Soda.**
1. Heat on platinum wire in alcohol flame	Colours the flame lilac	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.

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, each in a mild and caustic form (obtained by boiling with lime), were known, viz. :

(1) **Mild vegetable alkali** (potassium carbonate, K_2CO_3), obtained by the lixiviation of plant ashes : 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) . 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 putrefied urine, or from the *sal-ammoniac* of Egypt **caustic volatile alkali** (ammonium hydroxide, NH_4OH) described by Kunckel ("Laboratorium chymicum," published in 1716, fourteen years after his death).

According to the theory then held, limestone on burning absorbs *phlogiston* (ϕ), 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 :

$$\text{Mild alkali} + \phi = \text{caustic alkali}$$

This theory was irrevocably refuted as soon as the processes were studied with the aid of the balance

Black (who worked chiefly with magnesia, the mild form of which is easily decomposed by heat) found that when limestone is heated there is a loss of weight, and fixed air (CO_2, overlooked in the old theory) is disengaged. The residue is quicklime :

$$(1)\ \text{limestone} = \text{quicklime} + \text{fixed air.}$$

If the quicklime is boiled with a solution of mild alkali, the latter becomes caustic and the quicklime is converted into the original weight of limestone :

$$(2)\ \text{quicklime} + \text{mild alkali} = \text{limestone} + \text{caustic alkali.}$$

If we add equation (1) to equation (2), we find :

$$(3)\ \text{mild alkali} = \text{caustic alkali} + \text{fixed air.}$$

Hence the corrosiveness of quicklime and caustic alkali is an essential property of the pure earth and the pure alkali, respectively, and no "principle of causticity" is required.

The same fixed air was obtained by the action of an acid on both mild alkali and limestone, and the solution of limestone in an acid gave the original weight of limestone when precipitated by a mild alkali. No fixed air is evolved, as it is transferred from the mild alkali to the quicklime.

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.

The reactions involved in Black's researches are represented in modern symbols as follows

(1) *Preparation of quicklime from limestone* :

$$CaCO_3 = CaO + CO_2.$$

(2) *Slaking of quicklime* ·

$$CaO + H_2O = Ca(OH)_2.$$

(3) *Causticization of mild alkali*

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3.$$

(4) *Action of acid on limestone or mild alkali* :

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O;$$
$$K_2CO_3 + 2HCl = 2KCl + CO_2 + H_2O.$$

(5) *Precipitation of lime salt by mild alkali* :

$$CaCl_2 + K_2CO_3 = CaCO_3 + 2KCl.$$

Davy's isolation of the alkali-metals.—Previous to the researches of Davy the caustic alkalies were regarded as elements, although Lavoisier hinted that alkaline earths might be oxides of unknown metals. Humphry Davy (*b.* 1778–*d.* 1829), whose name is chiefly remembered 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 in 1807 to decompose the alkalies by electrolysis. The experiment succeeded.

"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 0·86).

(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 further experiments the metals called calcium, strontium, barium and magnesium, were prepared. 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. 1 —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. 112).

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

In the case of cupric oxide, for example, which dissolves readily in dilute sulphuric acid to form cupric sulphate, the solubility in water is so minute that, although the dissolved portion in a saturated solution is completely ionised, yet on account of the great dilution the total concentration of hydroxide ions never reaches the minimum value required to change the colour of the indicator. The neutralisation with acid follows the normal course, since the solution and ionisation of the basic hydroxide proceed as OH' ions are removed by the acid :

$$CuO\ (solid) + H_2O \rightleftharpoons Cu(OH)_2\ (dissd\ ) \rightleftharpoons Cu^{\cdot\cdot} + 2OH' ;$$
$$H^{\cdot} + OH' \rightleftharpoons H_2O.$$

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 504)

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 :

$$Al_2O_3 \text{ (solid)} + Aq. \rightleftharpoons 2Al(OH)_3\text{(dissd.)} \begin{cases} \rightleftharpoons H^{\cdot} + AlO_2' + H_2O \text{ (acid)} \\ \rightleftharpoons Al''' + 3OH' \text{ (base)} \end{cases}$$

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** (or **ampholyte**). Its salts with strong acids and strong bases are largely hydrolysed in solution (p. 322).

The composition of salts from acids and bases was first clearly expressed by Tachenius, who says (*Hippocrates chymicus*, 1666, p 11) : "Omnia salsa in duas dividuntur sunstantias, in alcali et acidum." This was the basis of the dualistic theory, and in another form appears in the modern ionic theory.

Sodium.

The alkali industry.—Sodium carbonate in a very impure state was formerly prepared by burning plants growing on the sea-shore (*Chenopodium*, *Salicornia*, *Salsola*, etc.), the ash being called *barilla* and 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 was, however, first satisfactorily effected by Nicolas Leblanc in 1787.

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 this 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 (sodium sulphate, Na_2SO_4),

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

the hydrochloric acid being absorbed and converted into chlorine, used in the manufacture of bleaching powder (p. 201). From the burnt pyrites, copper and sometimes silver and gold are extracted.

The salt-cake is now heated with carbon, in the presence of limestone, in *black-ash furnaces*. The reaction occurs in two stages, sodium sulphate being first reduced to sulphide:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2,$$

and the sulphide then reacting with the calcium carbonate to form a mixture of sodium carbonate and calcium sulphide, together with unchanged carbon and impurities, called *black ash*:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

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 351) of a cylinder of iron plates lined with firebricks, 15–20 ft long, running on rollers by means of bands on the outside of the cylinder.

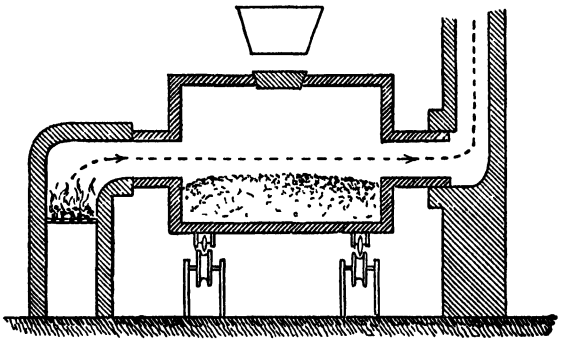


FIG 351.—Black ash revolving furnace.

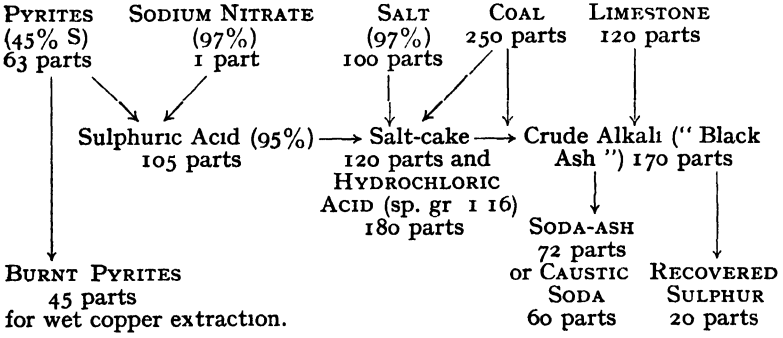
The rotation is effected by a cog-wheel passing around the cylinder, which engages with a smaller driving cog-wheel below. The firing is effected by producer gas made in a generator close to the furnace, the flame passing into the revolver through a fireclay ring called the "eye," hung between the end 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, 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 1¾ 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. 486). The liquors contain sodium carbonate, caustic soda, and impurities such as sodium sulphide and iron salts, they are worked up directly for the production of caustic soda, this process having been introduced in Lancashire in 1853 The Leblanc process is now almost obsolete

A diagrammatic scheme of the Leblanc process is given below



Caustic soda.—The Leblanc liquors (or solutions of sodium carbonate from the ammonia-soda process, *q v*) are run into *causticisers* (Fig. 352), 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 :

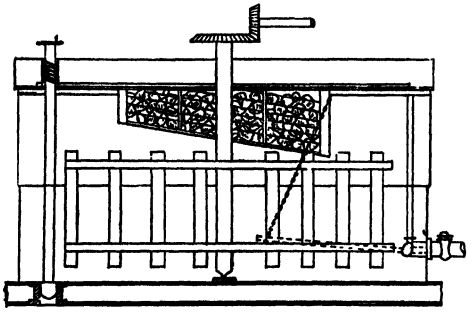


Fig 352.—Causticiser.

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3.$$

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 causticification, 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

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 Causticification 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 causticification is obtained

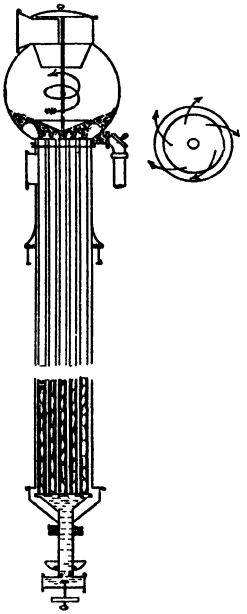


FIG 353.—Kestner vacuum evaporator.

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. The double salt *gaylussite*, $Na_2CO_3,CaCO_3,5H_2O$, which occurs native, may also be formed in the causticification process by the action of hot concentrated Na_2CO_3 solution on $CaCO_3$ The compound *pirssonite*, $Na_2CO_3,CaCO_3,2H_2O$, is similarly produced.

The causticised liquor is filtered from the lime sludge in a vacuum filter, and concentrated in vacuum evaporators. The liquid is heated under reduced pressure, when the boiling point is lowered.

The **Kestner evaporator** (Fig. 353) consists of a series of tubes in an outer jacket heated by steam. The liquid entering inside the tubes at the bottom under reduced pressure 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 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 fire until all the water is driven off and fused caustic soda remains. This is ladled out into iron drums, in which 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. Considerable quantities of caustic soda are now made by electrolytic processes (p. 204).

In purifying commercial caustic soda (or potash) containing chloride, carbonate and sulphate, it is treated 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 318·4°, 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 carbonate, Na_2CO_3, sparingly soluble in caustic soda solution, is formed. (Caustic potash does not resolidify, since potassium carbonate 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. 12·7°, have been described.

The densities D_4^{15} of caustic soda and potash solutions are given in the table :

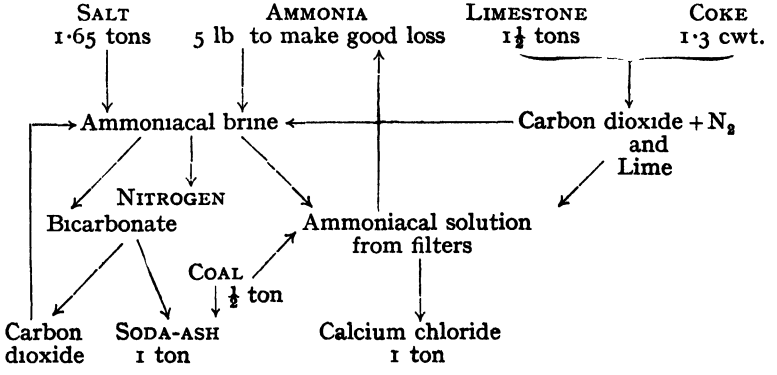
Per cent	Density NaOH	KOH
5	1·0555	1·0452
10	1·1111	1 0918
15	1 1665	1·1396
20	1·2219	1·1884
25	1·2770	1 2384
30	1 3310	1·2905
35	1 3835	1·3440
40	1 434	1·399
45	1 482	1·456
50	1·530	1·514

The ammonia-soda process.—In 1838 Dyar and Hemming in London 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 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 is still in use, even this is not essential The ammonia-soda process was introduced in 1874 by John Brunner and Ludwig Mond, at Winnington, near Northwich in Cheshire.

A diagrammatic scheme of the ammonia-soda process is given below :



The raw materials are common salt (or brine), limestone, coal and ammonia. These go through a cycle of operations which are carried on continuously day and night.

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.

This ammoniacal brine is treated with carbon dioxide, which is passed through under pressure in a *carbonating tower* (Fig. 354), 6 ft. in diameter and 70–90 ft high. This first converts the ammonia into carbonate.

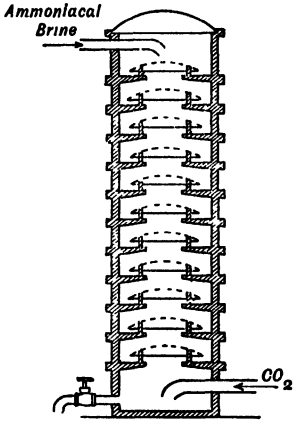


FIG 354.—Carbonating tower

$$2NH_3 + H_2O + CO_2 \rightleftharpoons (NH_4)_2CO_3,$$

and then tends to convert this into bicarbonate.

$$(NH_4)_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NH_4HCO_3$$

In proportion as ammonium bicarbonate is formed it reacts with the sodium chloride, giving by double decomposition **sodium bicarbonate**, $NaHCO_3$, and ammonium chloride.

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl$$

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. 554), and is treated with lime to recover the ammonia.

The bicarbonate is filtered and washed so as to free it as far as possible from ammonium salts, and is ignited to produce sodium carbonate and nearly pure carbon dioxide ("roaster CO_2").

The sodium bicarbonate from the filters is 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 *limekilns*, where the limestone is burnt mixed with coke to produce lime for the ammonia-stills, and the mixed gas is passed to the carbonating towers. Sodium carbonate, or *soda-ash*, issues from 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.

In the **Löwig process**, 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 over a free fire to produce fused caustic soda, which is ladled into iron drums.

Sodium carbonate.—Anhydrous sodium carbonate, technically 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 slowly dissolves. The solution is distinctly alkaline owing to hydrolysis. and on boiling slowly loses carbon dioxide: $Na_2CO_3 \rightleftharpoons 2Na + CO_3''$; $CO_3'' + H_2O \rightleftharpoons HCO_3' + OH'$. The percentage hydrolysis at 24·2° is (Shields) :

N	0·19	0·094	0·0477	0·0238
%	2·12	3·17	4·87	7·10

On evaporating the solution and cooling, large monoclinic crystals of *washing-soda*, $Na_2CO_3,10H_2O$, are deposited. These effloresce in air, forming a white powder of the monohydrate Na_2CO_3,H_2O, 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 are known, *e.g.*, two forms of $Na_2CO_3,7H_2O$, and unstable hydrates.

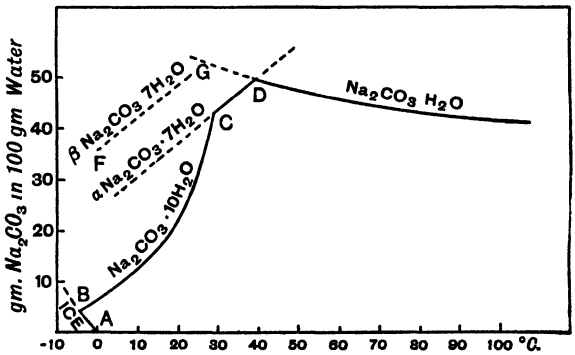


FIG. 355.—Solubility curves of sodium carbonate.

Solutions containing less than 6·3 g. Na_2CO_3 per 100 g. water deposit ice on cooling (curve *AB*, Fig. 355). *B* is the cryohydric point, at −2·1°, where ice, solid $Na_2CO_3,10H_2O$ and a solution containing 6·3 g. Na_2CO_3 per 100 g water coexist in equilibrium with vapour ($C=2$; $P=4$; $\therefore F=0$).

More concentrated solutions do not exist in *stable* equilibrium with ice and $Na_2CO_3,10H_2O$, yet a solution of 18·46 g. Na_2CO_3 in 100 g. water may on cooling become unsaturated with respect to decahydrate and deposits ice at −7·5°. *BC* is the stable part of the solubility curve of decahydrate (the ordinary " solubility curve "). At *C* the solid decahydrate changes into a rhombic heptahydrate, α-$Na_2CO_3,7H_2O$, at 32·00°. *CD* is the stable solubility curve of this salt, which may be prolonged on both sides into metastable regions, as shown by dotted lines. At *D* the heptahydrate changes into monohydrate, Na_2CO_3,H_2O at 35·37°, the solubility curve of which, with a prolongation into a metastable region shown dotted, is *DE*. Another heptahydrate, β-$Na_2CO_3,7H_2O$, which is always metastable, separates along *FG*.

Sodium bicarbonate.—This salt, $NaHCO_3$, 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, when saturated with carbon dioxide give a white crystalline powder 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 $[Na'] \times [HCO_3']$ 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 more 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, although this is much feebler than that of the carbonate: $HCO_3' + H_2O \rightleftharpoons OH' + H_2CO_3$. On heating the solution, carbon dioxide is 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.

If equimolecular amounts of sodium carbonate and 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 occurs as *trona* or *urao* in various localities, and is produced by the spontaneous evaporation of soda lakes, *e.g.*, in Egypt. The artificial salt, known as *concentrated soda crystals*, is used in wool-washing. It is neither efflorescent nor deliquescent. Large deposits of sesquicarbonate occur in lakes at Magadi, in British East Africa.

Sodium sulphates.—**Normal sodium sulphate**, Na_2SO_4, prepared in large quantities as *salt-cake* in the first part of the Leblanc process, 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 32·38°, but deposition of anhydrous salt simultaneously occurs. The solubility of Glauber's salt reaches a maximum at 32·38°. 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 32·38°, the first being the solubility curve of Glauber's salt, and the second that of anhydrous sodium sulphate (m. pt. 884°).

Glauber's salt readily shows the phenomenon of supersaturation If the supersaturated solution is brought in contact with a minute crystal of Glauber's salt, such as those floating in dusty air, crystallisation begins and Glauber's salt is deposited But if 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"), m pt. 185·7°, 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. A fused mixture or compound of this salt and the normal sulphate formed as a by-product in the manufacture of nitric acid, is known as *nitre-cake* The salts $NaHSO_4,H_2O$ and $Na_2SO_4,NaHSO_4$ are known The acid sulphate 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,** $Na_2S_2O_7$, m. pt. 400·9°, is formed on gentle ignition of the acid sulphate $2NaHSO_4 = Na_2S_2O_7 + H_2O$; by the action of sulphur trioxide on common salt: $2NaCl + 3SO_3 = Na_2S_2O_7 + SO_2Cl_2$; or (in the pure state) by the action of sulphur trioxide on the normal sulphate: $Na_2SO_4 + SO_3 = Na_2S_2O_7$. At a red heat it decomposes into sulphur trioxide and the normal sulphate. The solution of sodium hydrogen sulphate is acid: $NaHSO_4 \rightleftharpoons Na^{\cdot} + HSO_4' \rightleftharpoons Na^{\cdot} + H^{\cdot} + SO_4''$, but on evaporation above 50° it yields crystals of $NaHSO_4$.

Metallic sodium.—Although first prepared (Davy, 1807) from caustic soda by electrolysis: $2NaOH = 2Na + H_2$ (cathode) $+ O_2$ (anode), metallic sodium was for many years produced on the large scale by a process due to Castner (1886). In this, caustic soda was heated with carbon and iron at 1000°: $6NaOH + 2C = 2Na + 3H_2 + 2Na_2CO_3$. In 1890 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 is now produced by this method. The electrolysis of sodium chloride, mixed with potassium or calcium chloride or sodium fluoride, has been proposed.

The caustic soda is fused in a cylindrical iron pot (Fig. 356), and maintained at a temperature not higher than 330° by gas-burners A cylindrical iron cathode passes up through the base, and is sealed by solidified caustic soda into a prolongation of the pot The anode is a cylinder of nickel in electrical connection with a wire gauze cylinder surrounding the cathode The metal rises from the cathode, and floats on the surface of the caustic soda inside a small metal receptacle, provided with a lid 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

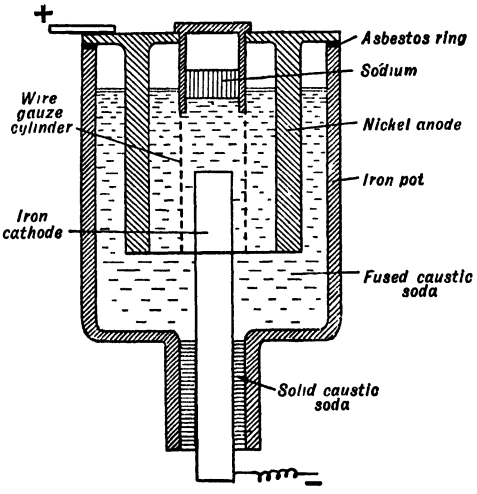


FIG 356 —Production of sodium by electrolysis.

Sodium is silver-white and soft, and 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. It burns when heated in moist oxygen or chlorine, and acts violently on water: $2Na + 2H_2O = 2NaOH + H_2$. It is a good conductor of electricity; its conductivity is about 33 per cent. that of silver (the best conductor).

Oxides of sodium.—Three oxides of sodium are known: **sodium monoxide**, Na_2O, a basic oxide; **sodium sesquioxide**, Na_2O_3, and **sodium peroxide**, Na_2O_2, or Na·O·O·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. The **sesquioxide**, Na_2O_3, is precipitated on passing oxygen through a solution of sodium in liquid ammonia.

Sodium peroxide, Na_2O_2, produced when the metal burns in excess of air or oxygen, is manufactured by heating sodium in aluminium trays in a current of purified air at 300° in iron pipes. It is yellow, becoming white on exposure to air from formation of sodium hydroxide and carbonate. 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: $Na_2O_2 + 2H_2O \rightleftharpoons 2NaOH + H_2O_2$, and 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 oxide shows powerful oxidising properties, converting chrome-ironstone (FeO,Cr_2O_3) into ferric oxide and soluble sodium chromate.

If 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.

When sodium peroxide is treated with absolute alcohol at 0°, a white powder of **sodium hydrogen peroxide**, Na O·O·H, is formed · $Na_2O_2 + EtOH = NaOEt + NaO{\cdot}OH$. It explodes on heating, evolving oxygen and forming caustic soda. A stable compound, $2NaHO_2,H_2O_2$, is formed on mixing 30 per cent hydrogen peroxide with sodium ethoxide (NaOEt) and absolute alcohol, or by the action of an ether solution of H_2O_2 on sodium Potassium forms $2KHO_2,H_2O_2$

Sodium hydride.—Sodium hydride is prepared by passing a slow stream of dry hydrogen over sodium in a nickel boat, heated in a glass tube at 365°. Colourless matted crystals form on the upper cooler portion of the tube just beyond the boat. It is decomposed by water with evolution of hydrogen: $NaH + H_2O = NaOH + H_2$, and by concentrated sulphuric acid with formation of sulphur and hydrogen sulphide. At 330° 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.—This salt is formed by heating sodium ferrocyanide, alone or with sodium: $Na_4Fe(CN)_6 = 4NaCN + Fe + 2C + N_2$ or $Na_4Fe(CN)_6 + 2Na = 6NaCN + Fe$. The pure cyanide, m. pt. 563·7°, is precipitated by passing hydrocyanic acid gas into alcoholic 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:

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$
$$2NaNH_2 + C = CN{\cdot}N{:}Na_2 + 2H_2.$$
$$CN{\cdot}N{:}Na_2 + C = 2NaCN.$$

Sodium cyanide is hydrolysed in aqueous solution: $NaCN + H_2O \rightleftharpoons NaOH + HCN$

Sodium silicate.—Sodium silicate (soluble glass) is made by melting together sodium carbonate and powdered quartz or pure sand in a reverberatory furnace at a high temperature. Probably various silicates are formed, *e g*:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

A mixture of sodium sulphate (*saltcake*) and powdered charcoal may be substituted for sodium carbonate, as in the manufacture of ordinary glass (*q.v.*):

$$Na_2SO_4 + 2C = Na_2S + 2CO_2;$$
$$Na_2S + 3Na_2SO_4 + 4SiO_2 = 4Na_2SiO_3 + 4SO_2.$$

The product is a greenish-blue glass (brown if sodium sulphide is present), which when broken up and heated with water under pressure in autoclaves is slowly dissolved to form a thick solution known as *water glass*, which may contain 2 to 4 molecules of SiO_2 to 1 molecule of Na_2O. It is strongly alkaline, and is used in treating cement floors to reduce dust and abrasion, for preserving eggs, and other purposes.

Sodium in analysis.—Sodium compounds give an intense yellow flame, which on examination by the spectroscope shows two yellow lines, very close together, known as the D-line; the wave-lengths are 5896 and 5890 A.U. A yellow precipitate of sodium zinc uranyl acetate, $NaZn_2(UO_2)_2(C_2H_3O_2)_9$, is produced by zinc uranyl acetate (p. 941) in neutral solution, from which potassium salts have been precipitated by zinc perchlorate. White sparingly soluble precipitates of the sodium salts are formed when hydrofluosilicic acid, potassium pyroantimoniate or potassium dihydroxytartrate are added to fairly concentrated solutions of sodium compounds.

POTASSIUM.

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; granite contains 1·7 to 3·1 per cent. of potassium, mainly in the form of *orthoclase felspar*: $K_2O,Al_2O_3,6SiO_2$. *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. 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 salts of organic acids occur: *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**, $KHC_4H_4O_6$, "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. In order to keep up the fertility of the soil, potassium compounds must be supplied; they are therefore essential 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 (3·5 : 1). The perspiration of the sheep is rich in potassium salts of organic acids. 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 compounds are widely distributed, *e.g.*, as felspar, comparatively few workable deposits of salts occur. The principal are at Stassfurt, in Saxony, at Mulhouse, in Alsace; and, in lesser amounts, at Cardona, in Spain, 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:

Upper 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 (at 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 deposits is *carnallite*, $KCl,MgCl_2,6H_2O$, which contains when pure 14·0 per cent. of potassium. The Alsatian and Galician deposits contain *sylvine*, a mixture of sodium and potassium chlorides richer in potassium than carnallite. The *kainite*, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, of Stassfurt is not worked to any extent.

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.

Potassium carbonate.—From the chloride, the sulphate and carbonate are prepared by a modification of the Leblanc process.

The charge for the black-ash furnace 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. $3(MgCO_3,3H_2O) + 2KCl\ aq + CO_2 = 2(MgCO_3,KHCO_3,4H_2O) + MgCl_2\ aq$ This solid is heated at 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 (*pearlash*), is a white deliquescent powder, m pt. 900°, dissolving readily in water to form a strongly alkaline solution. $K_2CO_3 + H_2O \rightleftharpoons KHCO_3 + KOH$.

One hundred parts of water dissolve:

Temp.	0°	26°	40°	60°	80°	135° (b. pt. sat. sol)
K_2CO_3	105	113·5	117	127	140	205

It 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.

A saturated solution of potassium carbonate readily absorbs carbon dioxide and deposits monoclinic crystals of **potassium hydrogen carbonate** or "potassium bicarbonate," $KHCO_3$ (or $K_2O,2CO_2,H_2O$),

easily prepared by passing carbon dioxide over moistened potassium carbonate and drying on a porous plate. It is much less soluble in water than the normal carbonate · at 10°, 27·7, and at 60°, 60 parts of $KHCO_3$, dissolve in 100 of water.

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

Potassium hydroxide.—Caustic potash, m pt. 360·4°, prepared in a similar manner to caustic soda, which it resembles closely in its properties, is made on the large scale by the electrolysis of potassium chloride solution 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.—This salt, KCl, occurs in cubic crystals as *sylvine*, melts at 790°, and is easily soluble in water : the solubility is 28 at 0°, 32·7 at 15° and 56·5 at 100°, increasing almost linearly with temperature. The salt is made from carnallite as previously described, and is used as a fertiliser.

The **bromide**, KBr, m pt 750°, and **iodide**, KI, m pt 705°, prepared as previously described, form cubic crystals and are used in medicine and photography. The **fluorides** KF (m. pt. 885°), KHF_2, KH_2F_3, and KH_3F_4 are known.

Potassium sulphates.—When 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 increases almost linearly with the temperature (Fig. 56). Potassium sulphate melts at 1050°.

The salt occurs in large quantities in double salts of the Stassfurt potash deposits : *schonite*, $K_2SO_4,MgSO_4,6H_2O$; 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 $K^{\cdot},Mg^{\cdot\cdot},SO_4^{\prime\prime},Cl^{\prime}$. 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 *schonite* 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 sparingly soluble potassium sulphate separates first, followed by *carnallite*, $KCl,MgCl_2,6H_2O$, from which KCl and $MgCl_2$ can be prepared.

Potassium sulphate is made 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 and permanganate. It is used in the preparation of potash alum and as a fertiliser, especially for tobacco.

If potassium sulphate is heated with an equivalent of concentrated sulphuric acid, it dissolves ; **potassium hydrogen sulphate** (" potassium bisulphate," $K_2O,2SO_3,H_2O$ or " acid potassium sulphate "), $KHSO_4$, being formed, m. pt. 197° (Roulle, 1754). This is obtained as a by-product in the preparation of nitric acid. It is readily soluble in water, the solution giving a strongly acid reaction : $KHSO_4 \rightleftharpoons K^{\cdot} + HSO_4'$; $HSO_4' \rightleftharpoons H^{\cdot} + SO_4''$.

On evaporation the solution, in accordance with van't Hoff's rule, deposits the normal sulphate, K_2SO_4, which is the salt with which it first becomes saturated. The residual solution contains free sulphuric acid. From it, 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 also known.

At a red heat, potassium hydrogen sulphate loses water and forms **potassium pyrosulphate**, m. pt. 414·2° : $2KHSO_4 = H_2O + K_2S_2O_7$. At higher temperatures this evolves sulphur trioxide : $K_2S_2O_7 = K_2SO_4 + SO_3$; 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. Since loss of water on heating $KHSO_4$ is incomplete even in a vacuum, the pure pyrosulphate is best obtained from sulphur trioxide and potassium sulphate.

Potassium phosphate, K_3PO_4, formed by heating a phosphate or phosphatic slag with coke and potassium sulphate, 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.

Potassium in analysis.—Potassium forms sparingly soluble salts with perchloric, hydrofluosilicic, chloroplatinic, tartaric and picric acids, all of which, together with sodium cobaltinitrite, 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 lilac flame coloration and the spectrum are also useful as tests.

Potassium cyanide.—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 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 pure.

Very pure cyanide, m pt 634·5°, is obtained by recrystallising from anhydrous liquid ammonia. The **cyanate**, KCNO, is obtained by fusing the cyanide with lead oxide: $KCN + PbO = KCNO + Pb$, 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, m. pt. 161°, is formed by fusing a mixture of potassium ferrocyanide and carbonate with sulphur. It occurs in traces in saliva **Potassium hydride**, KH, and **amide**, KNH_2 (m pt 271°), are formed similarly to the sodium compounds.

Potassium.—The metal is prepared in a similar way to sodium by the electrolysis of fused caustic potash, although the operation is difficult to carry out.

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 heated with a Bunsen burner placed on the anode side, so that a solid crust forms over the cathode. A globule of potassium forms under the crust.

Metallic potassium was formerly prepared by heating a mixture of the carbonate with charcoal to whiteness in an iron bottle, and cooling the vapour rapidly in a flat iron condenser: $K_2CO_3 + 2C = 2K + 3CO$. Unless the cooling is rapid, reaction of potassium with carbon monoxide occurred, with the formation of a yellow compound, $C_6O_6K_6$, which on exposure to moist air forms very explosive substances.

Potassium can 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, kept 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, becoming covered at first with a blue film. It acts violently on water, the liberated hydrogen burning with a lilac coloured flame. 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 occurs in traces in some blue specimens of sylvine, which contain small quantities of helium and neon.

An alloy of sodium and potassium is liquid at room temperature and resembles mercury, but is very easily oxidised, with evolution of heat and light, on exposure to air If a little chloroform or carbon tetrachloride is poured on a few drops of the alloy in a test-tube and, after fifteen seconds, the tube allowed to fall to the ground, the mixture explodes violently, alkali chlorides and carbon being formed.

Oxides of potassium.—**Potassium monoxide,** K_2O, and **sesquioxide,** K_2O_3, are prepared in a similar manner to the sodium compounds and have similar properties (K_2O is light yellow). **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.

Potassium and sodium sulphides.—Potassium and sodium burn when heated in sulphur vapour, forming mixtures of sulphides. By using excess of metal and heating the product in a vacuum, the pure monosulphides remain in cubic crystals. 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 hydrogen sulphide 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 hydrogen sulphide on solutions of sodium or potassium in ethyl alcohol, containing ethoxides: $NaOC_2H_5 + H_2S = NaHS + C_2H_5OH$.

If to a solution of caustic potash or soda which has been saturated with hydrogen sulphide, 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 shows 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	—

Lithium sulphide, Li_2S, does not easily form Li_2S_2, and no higher polysulphides of lithium are known.

LITHIUM.

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*, $(Li,K,Na)_2Al_2(SiO_3)_3(F,OH)_2$; *amblygonite*, an aluminium lithium phosphate (2·4–3 per cent. Li); 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 many minerals and 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 lithium bromide containing 10 per cent. of lithium chloride. It 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 (180°) is higher.

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 carbonate and sulphate, extract with water, precipitate the filtrate with barium chloride, and evaporate to dryness. 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 white **monoxide** (*lithia*), Li_2O, 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 below 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.* $Ca(HCO_3)_2$] The solution of the bicarbonate is called *lithia water*. On heating the normal carbonate in hydrogen at 780° it decomposes completely into the oxide and carbon dioxide (*cf.* $CaCO_3$) 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 is soluble in alcohol

Lithium salts give a 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 A.U.), and a brilliant crimson line (6708 A U). 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 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 . $Li_2C_2 + 2H_2O = 2LiOH + C_2H_2$. Fused LiH on electrolysis gives H_2 at the *anode*

Rubidium and **caesium** occur in very small quantities in certain mineral waters (*e.g.*, Durkheim, 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 caesium salts are not, and act as vegetable poisons. These two elements were the first to be discovered by the spectroscope (Bunsen, 1860–61). They give reddish-lilac and blue flame colours, respectively (Latin, *rubidus* = darkest red ; and *caesius* = the blue colour of the sky). They also occur in lepidolite, and some rare minerals. Carnallite contains about 0·035

per cent. of RbCl, which collects in the mother liquor from the preparation of potassium chloride The richest source of caesium is the rare silicate mineral *pollux*, found on the island of Elba

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 : the amounts in gm. of salts dissolved by 100 c.c. of water at 20° are :

	K	Rb	Cs.
Alums - - - -	13·5	2·27	0·619
R_2PtCl_6 - - - -	1·12	0·141	0·070

Caesium carbonate is soluble in alcohol, rubidium carbonate is practically insoluble

Rubidium salts are widely distributed, although in small amounts, but caesium 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 caesium have been mentioned (p. 751).

Ammonium (NH_4).

Ammonium compounds.—Ammonia, NH_3, readily combines with acids to form salts. Lavoisier regarded these as containing ammonia and the acids ; on this view, extended by Dumas in 1828, sal-ammoniac is *ammonia hydrochloride*, NH_3,HCl. Ampere (1816), however, supported the theory put forward by Davy in 1808, that the salts contain the **ammonium** radical, NH_4, which behaves as an alkali-metal. Salammoniac is *ammonium chloride*, NH_4Cl, analogous to potassium chloride, KCl. This view was favoured by Berzelius in 1820.

The ammonium theory had its origin in the discovery of **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. 125), the mercury 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 : $2NH_4 = H_2 + 2NH_3$. Davy (1808) 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 : $K + NH_4Cl = KCl + NH_4$.

Expt. 2.—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 that when ammonium amalgam is compressed in a tube under a piston it obeyed Boyle's law, and he concluded that it

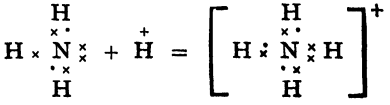
was simply a froth of hydrogen and ammonia gases in mercury. Pfeil and Lippman found that a similar amalgam was formed from salts of trimethylamine, *e g*, $N(CH_3)_4Cl$—tetramethylammonium chloride, whereas aniline salts, containing *liquid* aniline, $C_6H_5NH_2$, did not react The methylamine salts 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 tetramethyl-ammonium 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 merely colloidal solutions of the metals, the latter can be filtered out under pressure

According to Schlubach and Ballauf (1921) a colourless solution of free ammonium is obtained by adding the blue solution of sodium in liquid ammonia to a solution of ammonium iodide in the same solvent at −70°. $Na + NH_4I = NaI + NH_4$. At −40° this decomposes $2NH_4 = 2NH_3 + H_2$.

Although there is no doubt as to the existence of the **ammonium ion**, NH_4^+, 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.

The ammonium salts were formerly regarded as compounds of quinquevalent nitrogen, *e g.*, $(H_4) \equiv N—Cl$ It is now considered that the ammonium ion is formed by the addition of the neutral ammonia molecule to the hydrogen ion (proton), which remains univalent so that the whole ammonium ion is also univalent. The proton is linked by the lone pair of electrons on the nitrogen atom :



The four hydrogens are similarly attached to the nitrogen at the corners of a tetrahedron with nitrogen at the centre. If four different groups are substituted, $R_1R_2R_3R_4N$, the ion becomes assymmetric and optically active (Mills and Warren, 1925). In ammonium salts the NH_4 ions form a lattice with negative ions, *e.g.*, $NH_4^+ + Cl'$:

$$NH_3 + H^+ + Cl' = [NH_4]^+ + Cl'.$$

The NH_4 ion contains three ordinary covalencies and one semipolar double bond. The valency of the ion is polar, as the salts contain separate ions.

Ammonium chloride.—This compound, known as *salammoniac*, is prepared by neutralising ammonia with hydrochloric acid and evaporating, also by boiling a solution of ammonium sulphate, the commonest ammonium salt, 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 or by sublimation, by heating 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: *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, so that the crystals look like crystals of the hexagonal or tetragonal system. From a solution containing urea it crystallises in cubes. It exists in two forms, with a transition point at 184·5°.

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: $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl \rightleftharpoons NH_3 + H_2O + HCl$ Ammonium chloride vapour is dissociated: $NH_4Cl \rightleftharpoons NH_3 + HCl$, unless the salt has been carefully dried over P_2O_5, when it gives the normal vapour density corresponding with NH_4Cl. According to A. Smith and Calvert (1914–15) the *saturated* vapour of moist ammonium chloride is about 67 per cent. dissociated between 280° and 330°, and similar results were obtained with the other ammonium halides. The ready dissociation of the salt on heating explains its action as a flux in soldering: the oxides are converted into volatile chlorides by the hydrochloric acid, and a clean metal surface is left, *e.g.*:

$$CuO + 2NH_4Cl = CuCl_2 + 2NH_3 + H_2O.$$

Ammonium fluoride, NH_4F, **bromide,** NH_4Br, and **iodide,** NH_4I, are obtained by neutralising the corresponding acids with ammonia. The acid fluoride, NH_4F,HF, is also known.

Ammonium sulphides.—The formation of colourless needles and plates of **ammonium hydrosulphide,** NH_4HS, by mixing equal volumes of ammonia and hydrogen sulphide was described by Bineau in 1838 and confirmed by Bloxam in 1893. Bineau in 1839 stated that a

mixture of 2 vols. of ammonia with 1 vol of hydrogen sulphide at −18° gave mica-like crystals of **ammonium monosulphide**, $(NH_4)_2S$, but Bloxam found that these crystals always contain ammonium hydrosulphide, and although he says he obtained the monosulphide by carefully adjusting the volumes of the reacting gases and their rates of flow, the product was probably contaminated with hydrosulphide (Thomas and Riding, 1923). The pure hydrosulphide is precipitated in fine needles on passing alternately dry ammonia and dry hydrogen sulphide into dry ether. It dissociates rapidly and can be kept only in sealed vessels.

If hydrogen sulphide 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. 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 $(NH_4)_2S_5$ (see p. 497). By distilling a dry mixture of salammoniac, quicklime and sulphur, a blood-red liquid containing polysulphides is obtained, described by Basil Valentine. On prolonged exposure to air the solutions deposit sulphur, and form a colourless solution containing ammonium thiosulphate, $(NH_4)_2S_2O_3$.

Ammonium sulphate.—The manufacture of ammonium sulphate, $(NH_4)_2SO_4$, from ammonia has been described (p. 554). Instead of using sulphuric acid as absorbent, ammonia gas may be absorbed in a suspension of calcium sulphate (calcined gypsum), and carbon dioxide 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 forms large transparent crystals isomorphous with potassium sulphate and very soluble in water. On heating powdered ammonium sulphate it loses ammonia even below 100°, and at 300° is completely converted into molten **acid sulphate**: $(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$, which melts at 140° after solidification. At higher temperatures, decomposition with evolution of sulphur dioxide and nitrogen occurs. The acid sulphate is obtained in deliquescent crystals by dissolving the normal sulphate in hot concentrated sulphuric acid and cooling. The **sulphite**, $(NH_4)_2SO_3$, is obtained by passing sulphur dioxide through ammonia solution.

Ammonium nitrate.—This salt, first prepared by Glauber and called *nitrum flammans*, is obtained by neutralising 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: $NaNO_3 + NH_4HCO_3 \rightleftharpoons NH_4NO_3 + NaHCO_3$. A direct method of preparation has been described (p. 575).

The salt exists in five crystalline forms, with definite transition temperatures Tetragonal $\overset{-17^\circ}{\rightleftharpoons}$ (Rhombic)$_1$ $\overset{32\ 1^\circ}{\rightleftharpoons}$ (Rhombic)$_2$ $\overset{84\ 2^\circ}{\rightleftharpoons}$ Rhombohedral $\overset{125\ 2^\circ}{\rightleftharpoons}$ Cubic $\overset{169\ 6^\circ}{\rightleftharpoons}$ 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 and is also a constituent of explosives. A mixture (*amatol*) of 80 parts of ammonium nitrate and 20 parts of trinitrotoluene was extensively used in the late war.

Ammonium nitrite, NH_4NO_2, is obtained as an explosive deliquescent solid by passing the red gas from nitric acid and arsenious oxide (p. 585) through lumps of solid ammonium carbonate in a cooled tube, dissolving in alcohol, and precipitating with ether. It is formed by mixing the red gas 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 salt is now obtained by subliming a mixture of chalk and 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**, $NH_4O\ CO\ NH_2$.

If the solid is treated with alcohol the carbamate dissolves, leaving the bicarbonate, on exposure to air, the carbamate slowly volatilises: $NH_4O \cdot CO \cdot NH_2 \rightleftharpoons 2NH_3 + CO_2$, 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 it 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 digesting *sal volatile* 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

$$CO\begin{matrix}NH_2\\ONH_4\end{matrix} + H_2O \rightleftharpoons CO\begin{matrix}ONH_4\\ONH_4\end{matrix}$$

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

$$2NH_3 + CO_2 \rightleftharpoons NH_4O{\cdot}CO{\cdot}NH_2$$

Ammonium chlorate, NH_4ClO_3, is unstable and spontaneously explosive, solutions may explode violently on evaporation The **perchlorate,** NH_4ClO_4, is more stable but is endothermic and deflagrates with a yellow flame over 200° $2NH_4ClO_4 = N_2 + Cl_2 + 2O_2 + 4H_2O$. The **iodate** decomposes on heating $2NH_4IO_3 = N_2 + I_2 + O_2 + 4H_2O$ The nitrate deflagrates with a yellow flame when heated above 250° · $2NH_4NO_3 = N_2 + 2NO + 4H_2O$, at higher temperatures it detonates : $2NH_4NO_3 = 2N_2 + O_2 + 4H_2O$

CHAPTER XL

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. Co-ordination compounds containing bivalent silver are known (p 462) 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.*, $K[Ag(CN)_2]$.

	Copper	Silver	Gold
Atomic number	29	47	79
Electron configuration	2·8·18·1	2·8·18·18·1	2·8·18·32·18·1
Density	8·94	10·47	19·5
Atomic volume	7·12	10·3	10·2
Melting point	1083·0°	960·5°	1063·0°
Boiling point	2310°	1955°	2610°
Colour of vapour	green	blue	—
Oxides	Cu_4O? CuO Cu_2O CuO_2?	Ag_2O Ag_2O_2?	Au_2O Au_2O_2 Au_2O_3

Gold, with the highest atomic weight, differs in many respects from the other members of the group, this type of anomaly occurs elsewhere in the periodic system. Gold in many ways resembles platinum. Copper also shows a much closer relationship with mercury, which forms univalent and bivalent compounds, 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 k cal, are given below: the numbers for potassium are given for comparison:

R =	K	Cu	Ag	Au.
R + Cl	104 3	32 88	29 4	5 8
R + Br	95 6	25·0	22·7	−0·1
R + I	80 1	16 25	15·0	−5 5
R_2 + O	95·1	40 8	5·9	[Au_2O_3 − 12·3]

These values correspond approximately with the affinities of the various elements

COPPER.

Copper.—Copper occurs in the native or metallic state and many of its ores are easily reduced; it was therefore used in very early times, the oldest specimens of cast copper from Egypt and Babylonia dating to *c.* 4000 B.C. It appears later in the form of its alloy bronze, which contains copper and tin. Working in bronze was practised in Egypt at least as early as 2500 B.C.

Copper was obtained by the Greeks and Romans from the island of Cyprus, the Latin name *aes cyprium* or Cyprian copper afterwards became simply *cyprium*, and finally *cuprum* These names were, however, with the Greek *chalkos*, also used for brass and bronze The alchemists associated the metal with the planet Venus, and designated it by the symbol ♀. 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. It usually contains small quantities of silver, also bismuth and lead 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 copper is widely distributed, although in relatively small amounts, in the forms of *chalcocite* or *copper glance*, Cu_2S, and *covellite* or *indigo copper*, CuS, both probably formed by reduction of the sulphate by organic matter. The commonest ores of copper are *copper pyrites* or *chalcopyrite*, $CuFeS_2$, and *erubescite* (*bornite* 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.

Copper occurs in the red colouring matter (*turacin*) of the feathers of the plantain-eater (*touracus*), and in the *haemocyanin* of the blood of the cuttlefish, which acts like haemoglobin 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 Although the daily consumption of copper in food is about 1 mgm , it is said that as much as 100 mgm may be taken 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 to them. 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 algae, and a solution of copper sulphate mixed with slaked lime is used, as *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.

Native copper is 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 (*Manhès process*).

The Welsh process.—The separation of the iron and sulphur in the ore is difficult, since sulphur has a greater affinity for copper than for iron. On roasting, part of the copper and iron are oxidised, and arsenic present in the ore is volatilised as oxide. 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 fusible slag containing ferrous silicate, whilst the cuprous and iron sulphides form a lower layer, called *coarse metal* or *matte*.

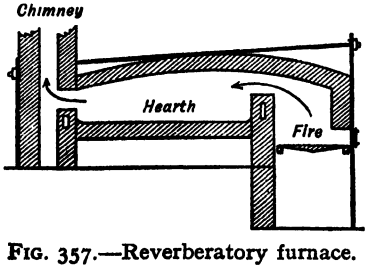


FIG. 357.—Reverberatory furnace.

Fig. 357 shows the section of a reverberatory furnace. The flames strike against the arched roof of the furnace and are deflected on to the charge on the hearth. The process is repeated with the matte and nearly pure cuprous sulphide, called *white* or *fine metal*, is obtained.

In the original process the blocks of fine metal are 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 oxidises impurities, *e.g.*, iron to FeO which forms a slag. Excess of Cu_2O would render the copper brittle, and is removed by covering the surface of the metal with powdered anthracite and stirring with a pole of green birchwood. Torrents of reducing gases bubble up through the metal, and the oxide is reduced. 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. The poled copper contains 0·02–0·04 per cent. of oxygen. If the reduction has been carried too far the metal becomes brittle, and is said to be *overpoled*. It is then exposed to the air in the molten state for a short time to allow it to recover its tough pitch.

In American practice the *white metal* is charged molten into a Bessemer converter (*q.v.*) and "blown." Very large reverberatory furnaces are usual in America (*e.g.*, at Anaconda), with sand hearths, and fired by gas, oil or powdered coal. They are displacing the blast furnace (see next section), as they are more suitable for powdered ore.

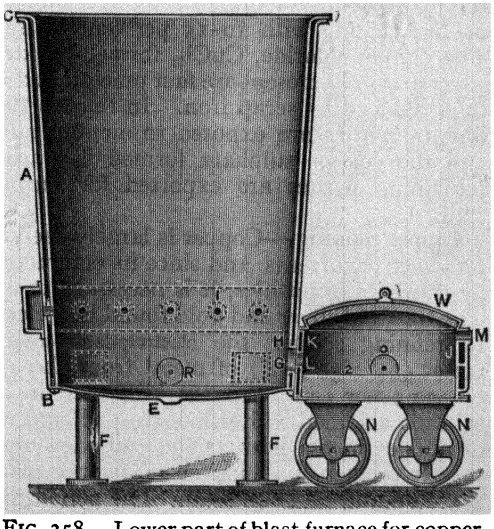


FIG. 358.—Lower part of blast furnace for copper.

The Manhès 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. 358). 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, 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 Bessemer **converter** (*q.v*) and a current of air is forced through it. This air is admitted through ports in an annular pipe above the bottom, as in Fig. 358, not through the bottom, as in steel-making (*q v.*). This modification, due to the French metallurgist Manhès (1880), is essential for success. The same reactions occur as in the Welsh process and copper is produced. Sulphur is burnt off as sulphur dioxide, iron passes into the slag as silicate, and arsenic etc. oxidise and 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 water-jacketted 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.

Copper is also extracted by **wet processes.** In one, the ore is leached with a solution of ferric sulphate, and a solution of copper sulphate is obtained which 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 first 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, to produce sulphuric acid.

Copper refining.—Copper is largely used in making wires and cables for 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 plates ($24'' \times 36'' \times 2''$) of metal from the converter or blister copper (98–99·5 per cent. Cu) 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 previously deposited on copper plates covered with a layer of graphite and oil (Fig. 359). The copper dissolves from the anode as cupric ions, $Cu^{\cdot\cdot}$; these travel to the cathode, where they give up their charges and are deposited as pure copper. Iron, nickel, cobalt, arsenic and zinc pass into solution as sulphates; gold, silver and any platinum metals (with some impurities, *e.g.*, selenium, tellurium and lead) fall as an *anode slime*, which is collected for the purpose of

obtaining the precious metals. The electrolytic copper is 99·96–99·99 per cent. pure.

A similar process (Jacobi 1837) is **electrotyping**. 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 plastic material and the latter covered with powdered graphite, a thin deposit of copper may be formed over

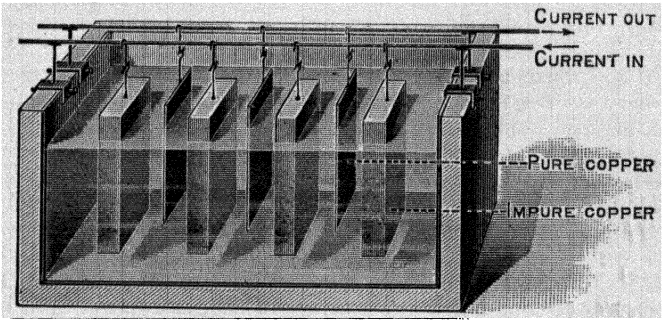


FIG. 359.—Purification of copper by electrolysis (diagrammatic).

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.

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 technical importance. *Brass* (copper + zinc) and *bronze* (copper + tin) were made at first 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. They are now made by fusing the copper, and adding the requisite amount of zinc or tin.

	Copper.	Tin	Zinc.	Iron.	Phosphorus
Brass - - -	4	—	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 Fe etc.	—
Dutch metal - -	80	—	20	—	—
Muntz metal - -	60	—	40	—	—
Old Roman coin -	96 06	—	2 71	0·85	—
Modern bronze coin	95	4	1	—	—

Casting bronze usually contains some zinc and lead. Bronze for machinery is 80–90 copper, 5–18 tin and 2–10 zinc. The best *brass* is 4 copper and 1 zinc; common brass contains 22–30 per cent. of zinc, but metal with 35–40 per cent. zinc can still be worked. *Silicon bronze* is used for telegraph wires. *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. *Monel metal* is 7 copper + 3 nickel.

Properties of copper.—A new surface of copper appears light red in colour, but the colour of copper produced by selective reflection is a deep rose-red, 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. 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 metal occlude various gases; when the metal solidifies these form bubbles, or give rise to "spitting" (*cf.* Ag).

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.

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.

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 air a green film of basic carbonate, sulphate or chloride (see p. 794) 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 red on the side in contact with the metal (cuprous oxide, Cu_2O). If heated for a long time in air, cupric oxide is formed. When heated in the oxyhydrogen blowpipe the metal burns with a very brilliant green flame.

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 when hydrated 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.—Cupric oxide or *black oxide of copper*, CuO, 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 1148°), but then evolves oxygen and leaves a solution of cuprous oxide, Cu_2O, in copper, which forms a solid mixture on cooling. Cupric oxide is readily reduced to metal by hydrogen, carbon or organic substances, when heated below redness The oxide dissolves in the borax bead, colouring it blue. If a little tin oxide 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 and cuprous oxides are used to give blue and red colours 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 yellow solution of cupric chloride, $CuCl_2$.

Cupric sulphate.—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 (Glauber, 1468): $Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$.

According to Cundall, the latter reaction leads first to the formation of **cuprous sulphate**, Cu_2SO_4, if the acid liquid is cooled, filtered through asbestos, and poured into water, a red precipitate of copper is formed $Cu_2SO_4 = CuSO_4 + Cu$ **Cuprous sulphide**, Cu_2S, is also formed, and deposits as a black powder in the earlier stages of the reaction, but is afterwards decomposed.

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

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

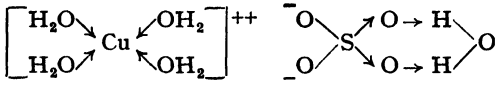
The final product is almost entirely $CuSO_4$ Other sets of equations have been proposed

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.

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. In blue vitriol, four molecules of water are supposed to be attached to the metal ion and one to the sulphate ion, in all cases by co-ordinate links:



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 are known. On exposure to air the blue pentahydrate crystals effloresce to a pale blue powder of $CuSO_4,3H_2O$. The crystals at 100° 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* or of *halhydration*, by Graham. Copper sulphate is stable up to 653° but at 736° is completely decomposed, leaving a residue of cupric oxide. 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.—Cupric sulphide, CuS, is a black solid formed by heating copper powder with excess of flowers of sulphur at a temperature below 440°, by the action of a solution of sulphur in CS_2 on copper powder, or by precipitating an acid solution of a cupric salt with hydrogen sulphide. 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 gently heated alone or in hydrogen : $2CuS = Cu_2S + S$.

Cupric nitrate.—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 and a hydrate with $9H_2O$ is known. On heating, the salt loses water and also nitric acid, forming a basic salt, $Cu(NO_3)_2,3Cu(OH)_2$, which is also precipitated from solution by ammonia. 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, $CuCl_2,2H_2O$, in hydrogen chloride gas at 150°. 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. 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 : $CuCl_2 \rightleftharpoons Cu^{\cdot\cdot} + 2Cl'$, the colour of the undissociated salt being yellow. A very dilute solution shows the pure blue colour of the hydrated cupric ion ; the green solutions probably contain a mixture of the blue ion and the yellow un-ionised

salt, although complex ions are also present, part of the copper being in anions, perhaps $CuCl_4''$. 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.

Cupric oxychloride, $CuCl_2,3Cu(OH)_2$, is formed as a pale blue precipitate when caustic potash is added to an excess of cupric chloride solution. It occurs in Atacama, Peru, Bolivia, etc., in the form of a crystalline green sand called *atacamite*, and 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 quicklime In solution, it shows the same colour changes as the chloride Cupric iodide is not stable in the solid state (see p 797).

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, is formed, insoluble in excess of alkali but soluble in ammonia. It appears that the precipitate, as stated by Berthollet, is a basic salt, *e.g.*, $CuSO_4,3Cu(OH)_2$. If a little of the copper solution is added to an excess of concentrated alkali, a deep blue colloidal solution is formed. If the pale blue hydroxide is boiled with water it becomes black, a hydrated oxide of the composition $4CuO,H_2O$, granular and easily filtered, being formed. On heating to redness this is converted into the oxide, CuO.

A crystalline hydroxide, $Cu(OH)_2$, is obtained by adding ammonia to a boiling solution of copper sulphate till the green precipitate becomes blue, washing, and digesting with fairly concentrated caustic soda solution at 20°–40°.

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 patina formed on copper exposed to air, usually described as the basic carbonate, is nearly always the basic sulphate, $CuSO_4$, $3Cu(OH)_2$, which occurs as the mineral *brochantite*, although occasionally the basic carbonate is present In places near the sea, or where salt spray is carried by the wind, the basic chloride $CuCl_2$,

$3Cu(OH)_2$ (*atacamite*) is formed. The definite compounds are formed only after a prolonged exposure of about 70 years. The sulphur dioxide content of London air varies from 0·08 to 0·4 (in fog) per million by volume; that in country air is about one-sixth of this.

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 at 70°. Basic phosphates occur as minerals. **Cupric 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 hydrogen phosphide 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 and telegraph wires **Cupric orthosilicates**, CuH_2SiO_4 and CuH_2SiO_4,H_2O, occur as the minerals *dioptase* and *chrysocolla*, respectively. The substance called "chrysocolla" by ancient authors was probably malachite

Copper peroxides of the (rather doubtful) formulae 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.—Red cuprous oxide, Cu_2O, is formed by the partial reduction of cupric compounds in the presence of alkalies.

EXPT. 1.—Dissolve 69 gm. of pure copper sulphate crystals in 1 litre of water, adding 1 drop of sulphuric acid. Call this *Solution A*. Dissolve in 1 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, perhaps of **cuprous hydroxide**, Cu(OH) is deposited, which quickly turns to bright red **cuprous oxide**, Cu_2O. 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*. When treated with dilute sulphuric acid, a solution of *cupric* sulphate is formed and metallic copper separates: $Cu_2O + H_2SO_4 = Cu_2SO_4 + H_2O = Cu + CuSO_4 + H_2O$. 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 or yellow on exposure to air, owing to oxidation and formation of cupric chloride: $4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O$. Cuprous chloride is soluble in sodium thiosulphate solution, and slightly soluble in caustic potash solution. The solution in hydrochloric acid is used in gas analysis for the absorption of carbon monoxide. The solution in ammonia, which is colourless if metallic copper is present, is used to absorb acetylene (see below).

Cuprous chloride.—By heating copper with mercuric chloride, Boyle (1666) 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 hydrogen chloride 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. 2.—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 Buchner funnel, and 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 425°, 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, $CuCl_2,3Cu(OH)_2,H_2O$. It dissolves readily in ammonia, forming a colourless solution of **cupro-ammine 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, $CuCl,CO,2H_2O$. 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 very insoluble white powder on addition of potassium iodide to a solution of cupric sulphate. Cupric iodide, first produced, is unstable and decomposes 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:

$$2CuSO_4 + 2FeSO_4 + 2KI = 2CuI + Fe_2(SO_4)_3 + K_2SO_4$$

EXPT. 3 Dissolve 10 gm. of blue vitriol and 12·5 gm of green vitriol in 250 c c of water and add 7 0 gm of KI in 75 c c of water. Filter, wash, and dry the 7·5 gm of Cu_2I_2 produced.

If the iodine liberated in the first reaction is titrated with thiosulphate, the **volumetric estimation of copper** is possible.

Excess of potassium iodide solution is added, and not more than 3 c c of concentrated HCl or H_2SO_4 or (best) 25 c c. of 50 per cent. acetic acid for 100 c c. of solution Starch is added when the yellow colour of the iodine is nearly discharged by the thiosulphate and titration continued till the colour is discharged. " After blueing " may occur on standing The solution should contain about 0·1 gm of copper in the volume titrated and 5 times as much KI as copper is added.

Cuprous sulphate is formed to some extent when cupric sulphate solution stands in contact with copper. $Cu + Cu \rightleftharpoons 2Cu^{\cdot}$ 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 160°, washing with ether, and drying *in vacuo*. It is at once decomposed by water, with deposition of copper. $Cu_2SO_4 = CuSO_4 + Cu$ **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. 4.—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.—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, CuCN, is formed. This dissolves in a solution of potassium cyanide, forming a colourless solution of **potassium cuprocyanide,** $K_3Cu(CN)_4$, which is a salt of a complex anion: $K_3Cu(CN)_4 \rightleftharpoons 3K^{\cdot} + Cu(CN)_4^{\cdot\cdot\cdot}$. Only traces of copper ions from the further ionisation: $Cu(CN)_4^{\cdot\cdot\cdot} \rightleftharpoons Cu^{\cdot} + 4CN'$, are formed, and the solution is not precipitated by hydrogen sulphide, since the concentration of copper ions is not sufficient to

exceed the solubility product of the very sparingly soluble cuprous sulphide. Cadmium sulphide, however, is precipitated if cadmium is present (see p 850). Potassium thiocyanate gives with a solution of cupric sulphate, to which ferrous sulphate or sulphur dioxide has been added, a very insoluble white precipitate of **cuprous thiocyanate**, CuCNS, insoluble in hydrochloric acid.

Cuprous hydride, CuH, is an unstable brownish-yellow precipitate obtained by reducing a solution of copper sulphate, acidified with a little sulphuric acid, with a hypophosphite at 70° It evolves hydrogen with concentrated hydrochloric acid. **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 (p 898), 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

Cupri-ammine 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 **cupri-ammine 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 **cupri-ammine sulphate**, $Cu(NH_3)_4SO_4,H_2O$, are deposited Cupric chloride forms **cupri-ammine 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.

Silver.—Silver was known in Predynastic Egypt (*c.* 4000 B.C.) but was very rare. A fine Chaldean silver vase of 2850 B.C. is in the Louvre. The alchemists associated silver with the 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, in presence of oxygen, of hydrogen sulphide in the air.

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 (*poisonous !*), 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). Much silver is obtained from the Ontario Cobalt Mines, from North America, Mexico, and Broken Hill (N.S. Wales).

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**), the silver-lead alloy being enriched by the **Pattinson process**;
(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**).

The **cupellation process** is the most ancient. It is described by Strabo and by Pliny as in use in Spain. 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 but it is now desilvered by the Pattinson or Parkes process (*q.v.*) The rich alloy is then melted on a flat dish called a **cupel** or *test*, formed of bone ash or (usually) of clay and limestone or barytes, or of cement (Fig. 360).

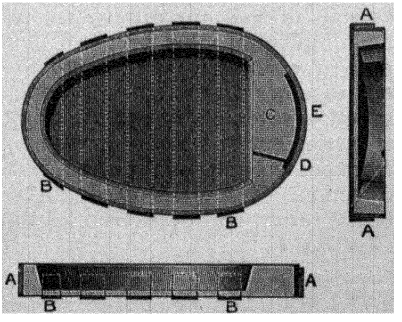


FIG. 360.—Cupel.

A blast of air is driven over the surface of the metal (Fig. 361). The lead is oxidised to lead monoxide or litharge, PbO, which fuses and is swept away by the air blast. The last portions of litharge are absorbed by the porous cupel, and a bright mass of silver is left.

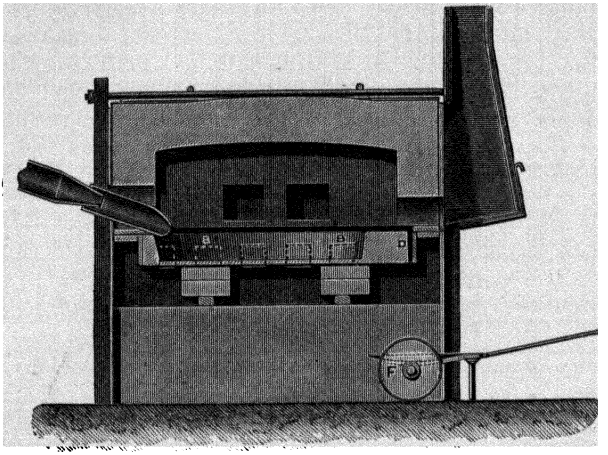


FIG. 361.—Cupellation furnace.

When the metal contains 60–70 per cent. Ag, the temperature is raised and a little sodium nitrate added to remove impurities. 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 and the metal contains 99·5 per cent. of silver.

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. 747). 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 (2·5 per cent. Ag ; 303° C.). In practice, seven-eighths of the original lead are 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 have separated, the liquid is strained off through a perforated plate The separated lead is remelted and the process repeated until the proportion of silver mechanically retained in the lead crystals is sufficiently small

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, one or two per cent of zinc is added to molten lead containing silver, the molten alloy of zinc and silver floats to the surface, and solidifies on cooling. A second lot of zinc is then added The crust 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 pure 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 and copper present are 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 If bismuth is present (which may be objectionable and is difficult to remove from the lead), it goes to the argentiferous part in the Pattinson process, but remains in the lead in the Parkes process, which is then less suitable

Amalgamation and wet processes.—The amalgamation process has been used in Mexico, where fuel is scarce; it was invented by a miner, Bartolomeo de Medina, in 1557. It has, since 1904, gradually been replaced by the cyanide process.

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, mixed with a little salt, 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: $2CuCl_2 + Ag_2S = 2AgCl + 2CuCl + S$; $2CuCl + Ag_2S = Cu_2S + 2AgCl$. 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 is distilled in iron retorts to recover the mercury

In the wet processes (*e g.*, Percy and Patera, Augustin, Ziervogel, etc.) 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. The anode slimes from copper refining are also roasted to convert the copper to sulphate, extracted with water (" leached "), and the residue cupelled or smelted in a basic reverberatory furnace with fluxes. In the modern **cyanide process**, as worked at Cobalt, Ontario, the unroasted ore or concentrate, 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 argentocyanide**, $NaAg(CN)_2$, is formed :

$$4Ag + 8NaCN + 2H_2O + O_2 = 4NaAg(CN)_2 + 4NaOH ;$$
$$Ag_2S + 4NaCN \rightleftharpoons 2NaAg(CN)_2 + Na_2S ;$$
$$2Na_2S + 2NaCN + O_2 + 2H_2O = 2NaCNS + 4NaOH$$

The silver is precipitated from the solution by sodium sulphide, and the silver sulphide reduced by caustic soda solution and aluminium ingots in a revolving cylinder.

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.

Silver alloys.—Commercial silver is alloyed with copper, because the pure metal is too soft for coinage or jewellery work. The proportion of silver in 1000 parts of alloy is called the *fineness*.

British silver coin since the time of Edward I. had a fineness of 925 ; in France, Germany, and Austria the silver coinage had a fineness of 900. The metal still retains the pure white colour of silver. The composition of the alloy used by the Mint is now 500 of silver, the remainder of the 1000 being principally nickel, with a little copper. Cadmium added to silver makes it easier to work as jewellery.

FIG. 362.—Cupel.

The **assay** of silver is made by heating a weighed portion of the alloy with a little pure lead on a bone-ash **cupel** (Fig. 362) in a **muffle furnace** (Fig. 363), 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.

Silver goods are often treated by heating in air; the copper in the alloy oxidises and 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.

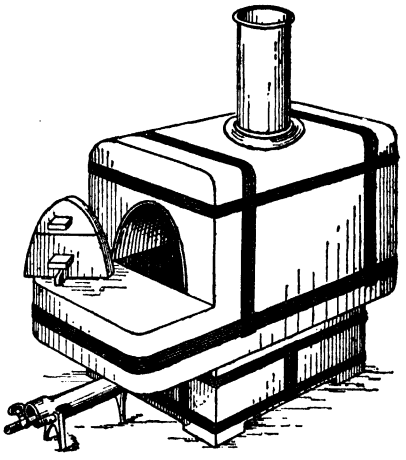


FIG. 363.—Muffle furnace for cupellation.

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 dry 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 moist silver chloride is boiled with caustic potash solution 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 moist silver chloride, and a stick of pure zinc placed in the mixture. The chloride is reduced, forming a grey mass of silver powder (*molecular silver*), which is washed and dried on a water-bath: $2AgCl + Zn = 2Ag + ZnCl_2$.

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 fusion on lime in an atmosphere of hydrogen.

Fused silver dissolves oxygen, which is liberated as soon as the metal begins to solidify. The solid crust is violently disturbed, and the metal " spits," part of the fused metal being forced out as globules or excrescences. This phenomenon, which is easily observed with the metal fused on a cupel, is a good test of the completion of cupellation. It is prevented by covering the metal with charcoal powder. Ten gm. of silver at 1020° dissolve 20·5 c.c. of oxygen (at S.T.P.).

Properties of silver.—Silver is a pure white metal which melts at 960·5° 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. 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 also transmit blue light.

In presence of dissolved oxygen, silver dissolves in distilled water to the extent of about 0·037 mgm. per litre, and about 0·003 mgm. more in a glass vessel: $2Ag + H_2O + O = 2Ag + 2OH'$. Silver is attacked by boiling concentrated sulphuric acid or cold dilute nitric acid, but resists the action of alkalies, even 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. 5.—Clean a test-tube with boiling nitric acid, wash well with water, and prepare in it a dilute 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 with ferrous sulphate in presence of sodium citrate, when a lilac precipitate is formed, which dissolves in pure water to form a red transparent solution.

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 and the X-rays show that the particles are crystalline (see *colloidal gold*, p. 814). 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

protargol or *collargol*. The colloidal modifications of silver do not conduct electricity; on heating, they 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: 1 ampere flowing for 1 sec deposits 0·001118 gm Ag.

One form of apparatus (Fig. 364) 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.

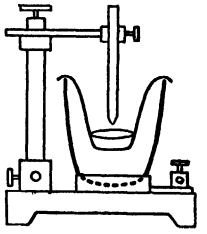


FIG 364.—Silver coulometer

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**: $KAg(CN)_2 \rightleftharpoons K^{\cdot} + Ag(CN)_2'$ 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 electroplating, copper goods were plated 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 electroplated goods. Copper plated with gold has been found in ancient Egyptian and Babylonian remains, and the later Roman coins were copper plated with silver

Compounds of silver.—Silver in its simple salts is univalent, but complex compounds of bivalent silver are known (p. 462). 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 formed. 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, with a solution of a chloride, insoluble in dilute nitric acid but readily soluble in ammonia, potassium cyanide or sodium thiosulphate. 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.—The most important salt of silver is the nitrate, $AgNO_3$, the preparation of which is described by 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, deep black in colour, so that a solution of silver nitrate is used as an indelible ink for marking linen. The black stain 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. It is soluble in alcohol.

Silver nitrate decomposes when strongly heated; oxygen and nitrogen dioxide are evolved and silver remains: $2AgNO_3 = 2Ag + 2NO_2 + O_2$. The decomposition point is much higher than that of copper nitrate, so that this may be separated from silver nitrate by heating, adding water, and filtering from the copper oxide.

Small quantities of copper may 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 is evaporated, crystals of a compound $AgNO_3,2NH_3$ separate. This is the nitrate of a complex cation, $Ag(NH_3)_2$ Double salts, *e g*, $AgNO_3,NH_4NO_3$ and $AgNO_3,KNO_3$, are known.

Silver nitrite, $AgNO_2$, is formed as a yellowish-white precipitate when solutions of silver nitrate and sodium nitrite are mixed. It may be crystallised from hot water. It decomposes on heating, evolving oxides of nitrogen and leaving silver nitrate and silver.

Silver oxide.—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 almost 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 slightly soluble in water (0·021 gm. per litre at 25°), 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 an alkali carbonate is added to a solution of silver nitrate. It loses carbon dioxide at 200°. With excess of potassium carbonate, a double carbonate, $KAgCO_3$, is formed as a white precipitate

Silver oxide gives off oxygen at 250° and is completely decomposed at 300°. It is used as a base and 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_3O_4(?), is deposited, mixed or combined with silver nitrate, on the anode in the electrolysis of silver nitrate with platinum electrodes It evolves oxygen on heating. Ag_2O_2 is said to be precipitated from $AgNO_3$ by potassium persulphate.

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 A subfluoride, Ag_2F, is formed by heating a solution of AgF with silver

Silver chloride, AgCl, occurs native as *horn-silver*, described by Conrad Gesner (1565) as *argentum cornu*, by Matthesius (1585) as "glass-ore, transparent like horn in a lantern," and as *luna cornea* by Oswald Croll (1608), who says it was used by the alchemists in the fraudulent transmutation of lead into silver. 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 455° it fuses to a dark-yellow liquid, which solidifies on cooling to a soft, colourless, tough mass. 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. 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 $2AgCl,3NH_3$ The thiosulphate solution contains a stable **sodium silver thiosulphate,** $Na_5[Ag_3(S_2O_3)_4] + 3H_2O$, which separates in crystals on adding alcohol or evaporation in a vacuum. It possesses a strong sweet taste.

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 a 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 ($N/10 = 16{\cdot}99$ 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. 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. Since it is more soluble than the chloride, the latter is first completely precipitated Another method is to add a little iron alum to the solution *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 and gives a red colour to the solution.

Silver bromide, AgBr, m.pt 422°, forms a pale yellow precipitate, insoluble (like the chloride) in dilute nitric acid, and only sparingly soluble in *dilute* ammonia but readily in concentrated. **Silver iodide,** AgI, m pt 556°, is produced as a light yellow precipitate, insoluble in dilute nitric acid and only very sparingly soluble in concentrated ammonia (which changes its colour to white). The solubilities in water of the halogen compounds of silver are as follows in mgm. per litre at 25°: silver chloride, 2; silver bromide, 0·133; silver iodide, 0·0023

Silver powder dissolves in aqueous hydriodic acid with evolution of hydrogen, on cooling, colourless crystals of AgI,HI separate, which rapidly decompose. Silver iodide is dimorphous and *contracts* on heating from −10° to 70° (Fizeau, 1867). Silver bromide does not absorb ammonia gas; liquid ammonia below 4° converts it into $AgBr,3NH_3$, decomposing at 4° into $2AgBr,3NH_3$. The iodide forms $2AgI,NH_3$ with ammonia gas, and AgI,NH_3 with liquid ammonia at −40°.

Silver chloride is not decomposed by cold concentrated sulphuric acid, but the boiling acid dissolves it· $2AgCl + H_2SO_4 = Ag_2SO_4 + 2HCl$. Hydrogen reduces heated silver chloride. $2AgCl + H_2 = 2Ag + 2HCl$.

Silver iodide is incompletely reduced by hydrogen, even at a very high temperature

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:

$$Ag_2O + H_2O \rightleftharpoons 2AgOH;$$
$$AgOH + Cl_2 = AgCl + HClO;$$
$$AgOH + HClO = AgClO + H_2O$$

In presence of silver oxide the hypochloride 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 at 150° (Stas). $3AgClO = 2AgCl + AgClO_3$. It melts at 230° and is decomposed at 270° into chloride, oxygen and a trace of chlorine. 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.—This salt, Ag_2SO_4, is formed by boiling silver with concentrated sulphuric acid, or by precipitating a solution of the nitrate with a sulphate. It is sparingly soluble in water (0·77 parts at 17° and 1·46 parts at 100°, in 100 water), but dissolves readily in dilute or concentrated sulphuric acid, or in dilute nitric acid. Silver sulphate begins to decompose at 917° and is completely reduced at 923°: $Ag_2SO_4 = 2Ag + SO_2 + O_2$. 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 in hydrogen sulphide, or silver nitrate is precipitated with the latter.

A **disulphide**, Ag_2S_2, is said to be 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 (solubility 6 mgm. per litre of water at 20°) when a solution of sodium phosphate is added to one of silver nitrate. The reaction is usually represented by the equation:

$$3AgNO_3 + Na_2HPO_4 = Ag_3PO_4 + 2NaNO_3 + NHO_3,$$

but as the precipitate is readily soluble in nitric acid, only about 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 light chocolate-brown, respectively, and are formed by precipitation. The former dissolves in ammonia, and if the solution is boiled silver is deposited. The solubilities of the arsenite and arsenate are 11·5 mgm. and 8·5 mgm. per litre at 20°, respectively.

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

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 upon 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 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, 1839) by immersion in a solution of a reducing agent such as 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. Positives were obtained by laying the negative on a piece of paper coated with silver chloride, and then exposing for some minutes to sunlight or bright daylight, when the chloride was sufficiently changed in colour to give a positive " print." The print could be fixed in the same way as the plate, when a yellowish silver image was left. The colour was much improved by immersing the print, before it was fixed, in a solution of gold chloride (brown to purple tones), or potassium platinochloride (grey tone), some of the silver being dissolved and replaced by the nobler metal.

In the modern process the light-sensitive medium is usually a suspension or " emulsion " of silver halide in gelatin. The halide used depends on the particular type of photographic material High-speed plates and films contain a mixture of bromide with a small proportion of iodide ; process plates, fast lantern plates and bromide papers contain bromide ; warm tone " chlorobromide " papers and lantern plates contain a mixture of chloride and bromide ; gaslight papers and lantern plates contain chloride. Self-toning print-out papers usually have a collodion emulsion containing silver chloride, silver citrate, gold chloride and citric acid. The various types of gelatin emulsion are prepared by adding silver nitrate to a solution of gelatin in hot water containing alkali halides in the required proportions. The warm emulsion, after " ripening " for some time, when the silver halide grains increase in size, is allowed to cool and set. The jelly is cut up, washed with water to remove soluble salts, and is then remelted and coated as a thin film on glass (for " plates "), celluloid (for " films "), or on paper having a specially prepared surface. All operations are carried out in the dark, or in light of a colour to which the photographic material is not sensitive. By adding certain dyes (" sensitizers ") to the photographic emulsion, it is possible to make it sensitive to rays which do not affect ordinary photographic materials : thus erythrosine makes the emulsion sensitive to yellow and green in addition to the blue and violet rays (" orthochromatic ") ; some cyanine derivatives confer sensitivity to the whole visible spectrum (" panchromatic ") and other cyanine derivatives make the emulsion sensitive to the near infra-red region, rays which are capable of penetrating fog and haze well enough to render long-distance photography possible.

After exposure in the camera, which may be only a small fraction of a second, the film or plate does not change in appearance, but in reality a change has occurred in the places on which light has fallen. It is *developed* by immersing in a solution of a reducing agent such as pyrogallol, hydroquinone, or metol, in the presence of alkali and sodium sulphite. The exposed silver halide is then reduced to black metallic silver : $C_6H_4(OH)_2 + 2AgBr = C_6H_4O_2 + 2Ag + 2HBr$.

To prevent over-vigorous development, when some of the unexposed halide is reduced and leads to " fogging " of the plate, potassium bromide is added to the developer. It retards development by lowering the solubility of the silver bromide or chloride. Desensitizers are dyes (usually of the safranine class) which when dissolved in the developer solution enable development to be carried out in fairly bright artificial light instead of the very dim red or green light usually employed. After washing, the film or plate is fixed in a solution of sodium thiosulphate. Positive prints are usually made on bromide or gaslight papers, which are exposed, developed, and fixed in the same way as plates

Sheppard (1925) found that the very high speed of photographic

emulsions is due to the presence of traces (1 part in 100,000 to 1 part in 300,000) of organic sulphur compounds present in the gelatin. The exact mechanism of the photochemical changes is still obscure According to one theory, a subhalide, *e.g.*, Ag_2Br is formed by the transfer of bromine to the sensitizer. 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 effect: AgBr > AgCl > AgI. Cathode rays (free electrons) and X-rays (which produce free electrons from matter) also produce photographic effects Sheppard and Trivelli (1926-1928) consider that minute nuclei of silver and silver sulphide (" sensitivity specks ") which are present in silver halide crystals, play an important part, electrolytic action being set up on exposure to light which enlarges the nuclei so that they may become centres of development Toy and Harrison (1928) found that the electrical conductivity of silver halides increases on exposure to light, and suggest that on exposure the halogen ions lose their extra electron, which is thus free to convert a silver ion to a silver atom. The quantum efficiency of the process (p 200) is 1 (Eggert and Noddack, 1923) the primary process is confined to the halide ion · $Hal' = Hal + \ominus$, followed by the secondary reaction $Ag^{\cdot} + \ominus = Ag$ According to Hamburger (1933) as few as three silver atoms, arranged as in the silver crystal lattice, are able to act as a centre from which development may proceed. It seems to be well established that photosensitivity depends to some extent on the nature of the adsorbed gelatin-silver or dye-silver complex on the surface of the halide crystals. Scheele's original experiments, however, prove conclusively that chemical reactions occur when the action of light is prolonged, and loss of chlorine with the formation of silver (not subhalide) has been established by experiments with the microbalance (Hartung, 1922-25) Up to 95% may be decomposed Rehalogenation restores the original weight and colour.

GOLD.

Gold.—Gold, by reason of its occurrence in the free state, and of its marked colour and brilliance, was probably one of the first metals known to man. Gold ornaments are found in neolithic remains. The metal was associated with the sun by the alchemists, and represented by the symbol ☉. The alchemists considered that the other metals, if suitably purified, could be transmuted into gold.

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, and traces of gold are found in pyrites and other ores, and in sea-water (less than $\frac{1}{10}$th grain per ton). Gold is recovered from burnt pyrites, but a sea-weed which collects gold instead of iodine is yet unknown.

The native gold occurs mainly in quartz veins or reefs intersecting metamorphic rocks, but is found also in many other formations, *e.g* the Lower Silurian in Wales, and even up to the chalk The most important European localities where gold is found are Russia and Hungary. Hungarian gold may contain tellurium, which must be separated if the metal is to be used for dental purposes The Russian mines of the Urals, opened 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 8,419,100 oz in 1918, and gives the highest production in the world) and in Australia. Gold occurs all over Asia. In North America the fields extend from Mexico to Klondike, the latter field being opened in 1896 *Electrum* is a native alloy of gold and silver, containing 15 to 45 per cent of silver; *green gold* contains 10 per cent. of silver These alloys were used in ancient Egypt and called *asem*. Australian gold sometimes contains an appreciable amount of silver

Metallurgy of gold.—Native gold occurs either in the rock as *nuggets* of varying size (one of 184 lb. weight was found at Ballarat), 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 100-300 ft. 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. Gold is only slightly soluble in mercury and the separation is due to adhesion (see p. 10). 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. 799).

To extract gold from auriferous pyrites, obtained from the rock as so-called "concentrates," they are treated by Percy and Plattner's **chlorine process** (1846) 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 is precipitated by reduction with ferrous sulphate or solid charcoal. Bromine water is also used instead of chlorine.

Gold is 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 (1887). In this way quartz containing only half an ounce of gold per ton can be profitably treated. The ore is percolated, or the slimes are agitated, in large tanks with a solution of cyanide containing the equivalent of 0·3 per cent. of KCN, in which the gold dissolves. After settling or filter-pressing, the clear liquor is reduced by adding charcoal or metallic zinc (of which metal the packages for the export of the cyanide are made). The precipitate is fused in plumbago crucibles, or is melted with lead, and the alloy containing 10 per cent. of gold cupelled. The reactions in the cyanide process are somewhat complicated; they occur in

presence of atmospheric oxygen, **potassium aurocyanide** dissolves and hydrogen peroxide is formed by autoxidation:

$$2Au + 4KCN + 2H_2O + O_2 = 2KAu(CN)_2 + 2KOH + H_2O_2;$$
$$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH;$$
$$2KAu(CN)_2 + Zn = K_2Zn(CN)_4 + 2Au.$$

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 (Scheffer, 1753).

The alloy must not contain more than 33 per cent of gold, otherwise the silver is not dissolved If it contains more gold the alloy is melted with silver until it contains about one-quarter its weight of gold This operation of separation is termed **quartation** Parting with boiling nitric acid, in which the silver is dissolved as nitrate from an alloy containing not less than 1 part of silver to 2 of gold, is an older process still used. It was used in Venice in the fifteenth century to separate the gold from Spanish silver

In the **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. In the **Miller process** (1869), used at the Ottawa Mint, chlorine gas is passed through the molten metal covered with borax. Silver chloride is formed and floats to the top.

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, as does 1 part of lead in 1000 of gold

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 (19·43),

and is a good conductor of heat and electricity. It melts at 1063°, expanding on fusion, and forms a bluish-green liquid (*cf.* copper, p. 790). It volatilises appreciably 100° above its melting-point, and boils at 2610°. It is the most ductile metal, as was stated by Pliny, and can be beaten into leaves 0·00009 mm. thick. Gold leaf was used on old Egyptian mummies. The ordinary leaf is 0·0001 mm. thick. The deposits on gold lace are only 0·000002 mm. thick Gold leaf transmits green light. On heating it at 316° the metal transmits red light; at 550° it crystallises and minute gaps are formed, which make it appear transparent 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* (1 part conc. HNO_3 +4 parts conc. HCl). Fused alkalies and nitrates, and a solution of ferric bromide, also attack it Gold differs from copper and silver in the extreme ease with which its compounds are reduced to the metal.

Colloidal gold is formed by Bredig's process (p. 804), or by reducing solutions of gold chloride with phosphorus, ferrous sulphate, hydrazine, formaldehyde, etc. The different solutions have different colours according to the sizes and shapes of the colloidal particles. Those with larger particles are blue; with decreasing size the colour passes to a fine ruby-red. Silver sols are deep yellow (conc) to lemon yellow (dil.), orange in presence of traces of copper; copper sols are red; bismuth sols are deep brown to yellow. In colloidal gold the particles are crystalline, as shown by the X-rays By precipitating gold chloride with a mixture of stannous and stannic chlorides, a purple powder called **purple of Cassius** (discovered by Andreas Cassius, and described by Orschall in 1684 and by Cassius' 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 it is colourless, but when annealed it assumes a fine ruby colour, due to the presence of ultramicroscopic particles of gold. Gold forms a purple alloy with aluminium, $AuAl_2$.

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**, $HAuCl_4,4H_2O$, which lose HCl at 120° to form **auric chloride**, $AuCl_3$. 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 is left, soluble in water, alcohol or 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 insoluble but is decomposed by water: $3AuCl = AuCl_3 + 2Au$. Chlorauric acid, when mixed with concentrated hydrochloric acid and potassium chloride, gives light yellow crystals of **potassium chloraurate**, $2KAuCl_4,H_2O$.

On heating, these form the **chloraurite**, $KAuCl_2$. AuCl, treated with cold dilute potash, gives a violet powder of **aurous hydroxide**, AuOH; on heating this at 200° **aurous oxide**, AuO, is said to be left, although Pollard (1926) says it is a mixture of gold and auric oxide. By heating $AuCl_3$ solution with magnesia and washing with dilute nitric acid, **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; with potassium bromide it forms $KAuBr_4$ in purple-red crystals. 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 as an amorphous black powder when anhydrous lithium aurichloride, $LiAuCl_4$, 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.

Fulminating gold is prepared by treating auric chloride solution with ammonia; it is an olive-green powder of variable composition which when dry explodes with great violence when heated or struck. The fulminating gold formed by digesting auric hydroxide with ammonia is $2AuNH{\cdot}NH_2,3H_2O$. 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.

Potassium aurocyanide, $KAu(CN)_2$, is produced by dissolving fulminating gold in boiling potassium cyanide solution On cooling, colourless lustrous crystals separate. When the solution in hydrochloric acid is evaporated and the residue washed it leaves yellow **aurous cyanide**, AuCN. Auric cyanide, $Au(CN)_3$, is not known, but **potassium auricyanide**, $KAu(CN)_4$, 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 boiling solution into concentrated stannous chloride solution.

CHAPTER XLI

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** : beryllium, magnesium, calcium, strontium, barium and radium.

(*b*) **Odd series** : zinc, cadmium and mercury.

In many ways beryllium and magnesium resemble more closely the metals of the (*b*) series, and will be dealt with in the next chapter. Radium has been described in Chapter XXV.

	Be	Mg	Ca	Sr	Ba
Atomic number -	2	12	20	38	56
Electron configuration	2·2	2·8·2	2·8·8·2	2·8·18 8 2	2 8·18·18·8·2
Density - - -	1 84	1 74	1 55	2 54	2 6
Atomic volume - -	4 90	1·40	25·9	34·5	36·2
Melting point - -	1350°	651°	810°	752°	658°
Boiling point - -	1500°	1380°	1712°	1639°	1810°

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 formulae Hg_2X_2, in which the group —Hg—Hg—, made up of two bivalent mercury atoms, is also bivalent. All these metals form stable basic oxides, RO, and (except mercury) hydroxides, $R(OH)_2$. There is a regular increase in the solubility of these hydroxides in series (*a*) ; those of series (*b*) are practically insoluble in water: gm. dissolved by 100 gm. of water at 20° : $Ca(OH)_2$, 0 163 , $Sr(OH)_2$, 0 81 ; $Ba(OH)_2$, 3·75

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 (1808) by electrolysis, following a suggestion by Lavoisier that, like other " bases," the earths were oxides of metals.

The metals of the alkaline earths are all silver-white, oxidise in the air and decompose water, though less vigorously than the alkali-metals. They form, in addition to the basic oxides, RO, true peroxides, RO_2, in which the metal is still bivalent: $R\begin{smallmatrix}O\\|\\O\end{smallmatrix}$ They unite directly with hydrogen and with nitrogen, forming hydrides, RH_2, and nitrides, R_3N_2, respectively. Their compounds give distinctive colours when moistened with hydrochloric acid and heated on platinum wire in the Bunsen flame: calcium, orange-red; strontium, crimson; barium, apple-green; radium, carmine-red.

Calcium.

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* (density 2·72) (Fig. 365), and in the

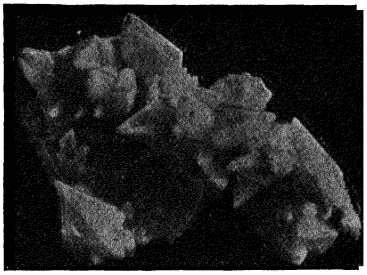


Fig. 365.—Calcite from Guanaxuato (*British Museum*).

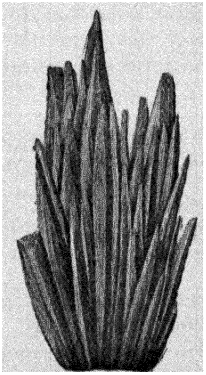


Fig. 366.—Aragonite from Cumberland (*British Museum*).

rhombic system as *aragonite* (density 2·92) (Fig. 366). Calcite is the common form; besides occurring in minerals, it forms the chief constituent of eggshells and bones (together with calcium phosphate), all of which effervesce with acids. Aragonite occurs in the shells of molluscs and in coral. In the massive form calcite 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 and pressure. Above 400° aragonite is transformed into calcite.

A third form, μ-$CaCO_3$, is said to be precipitated from lime-water at 60°. The solubility of calcium carbonate in water containing carbonic acid has already been described (p. 170). By adding a solution of $KHCO_3$ to a cooled solution of $CaCl_2$, a white precipitate of $Ca(HCO_3)_2$ is formed Kohlrausch states that 1 litre of water dissolves 13 mgm. of calcite and 19 mgm. of aragonite, at 18°. In presence of carbon dioxide 100 times as much calcite dissolves. When boiled for a few minutes with cobalt nitrate solution, aragonite is coloured violet but calcite is unchanged An unstable hexahydrate, $CaCO_3,6H_2O$, is formed by the action of carbon dioxide on solutions of lime in sugar solutions.

Quicklime.—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

$t°$ C	-	-	- 500	600	700	800	898	900	950
Pco_2 mm. Hg.			- 0·11	2·35	25·3	168	760	773	1490

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 being known as lime-burning. Decomposition occurs still more easily in a current of steam.

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. 367) 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 continuous limekilns are now used. The lime works its way gradually down the kiln, which may be fired by producer gas, and is withdrawn at the base.

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 2570° 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 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.

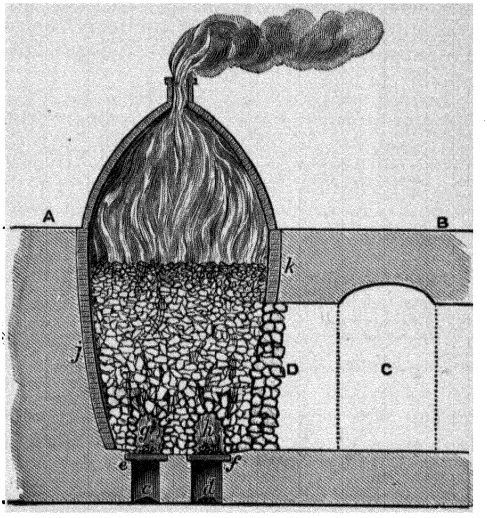


FIG. 367.—Derbyshire limekiln.

Slaked lime.—If quicklime is moistened with water, much heat is evolved and clouds of steam are given off: $CaO + H_2O = Ca(OH)_2 +$ 15·54 k. cal. (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 quicklime is mixed with a sufficient excess of water a paste is formed; if shaken with water this forms a suspension called *milk of lime*; the hydroxide dissolves sparingly, producing *lime-water* (1·29 gm. of CaO per litre at 15°; 0·67 at 80°). The solubility, as Dalton found, decreases with rise of temperature.

Calcium hydroxide is 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 Francesco 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: $Ca(OH)_2 \rightleftharpoons CaO + H_2O$. The dissociation pressures are 100 mm. at 350° and 760 mm. at 450°. A hydrate $Ca(OH)_2,H_2O$ has been described.

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 quicklime does not absorb dry carbon dioxide, nor does it react in the cold with chlorine, hydrogen sulphide, sulphur dioxide or nitrogen dioxide; hydrogen chloride reacts only slowly. 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 gives a powdery mixture with water; it is called "poor lime," as distinguished from "fat lime," which gives a paste with water. The hardening of mortar consists in the evaporation of the moisture, or its absorption by the bricks, and

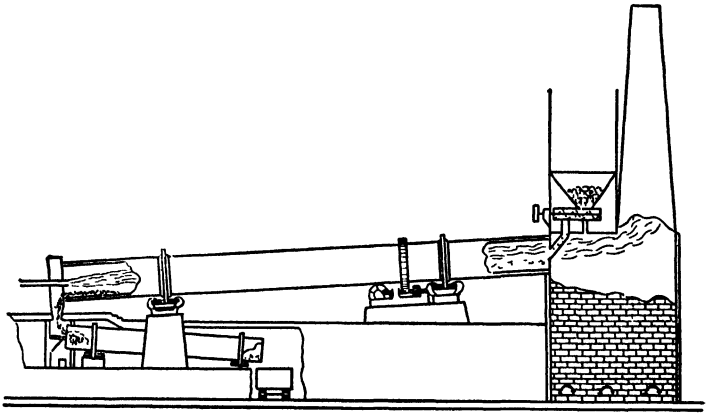


FIG 368.—Cement furnace

the slow conversion of the hydroxide into calcium carbonate by atmospheric carbon dioxide; no combination between the lime and the silica of the sand occurs, these substances reacting only above 620° at an appreciable rate (Huttig and Rosencranz, 1929). Modern mortar usually contains ground clinkers 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*. Vitruvius says the Romans used both lime mortar and a hydraulic mortar for harbour works.

In 1796 James Parker prepared a similar *Roman cement* by heating clay and limestone below the sintering point. *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 (Fig 368). The materials sinter, and 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, and according to Rohland not less than 3 per cent of ferric oxide 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 crystallised in the form of a mass of interlacing needles of the basic silicate Michaelis, however, considers 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.

Calcium chloride.—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 at 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 782°, and forms a hard crystalline mass on cooling The product contains a little free lime unless fused in hydrogen chloride gas. 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; at 260°, anhydrous $CaCl_2$ (Roozeboom, 1889). An oxychloride is said to be formed in needles by boiling the hydroxide with calcium chloride solution.

Large quantities of calcium chloride are formed as a by-product of the ammonia-soda process; a solution of it is used in refrigerating plants (as " brine "), since it freezes only at a low temperature.

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°) is nearly insoluble in water (15 mgm. per litre at 18°); it is more soluble in ammonia, ammonium salts and acids. When heated on charcoal before the blowpipe it evolves HF and leaves CaO. The **bromide**, $CaBr_2$ (m. pt. 730°), and **iodide**, CaI_2 (m. pt. 740°), are similar to the chloride. The bromide forms $CaBr_2,6H_2O$ and the iodide hydrates with 6 and $8H_2O$. CaI_4 is said to be formed by heating CaI_2 and iodine at 70°–80°, and in solution.

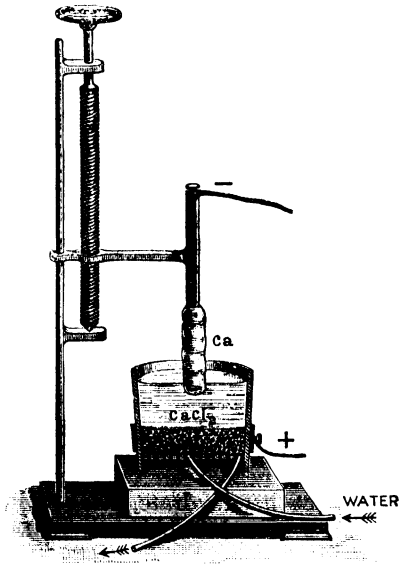


FIG. 369.—Calcium by electrolysis.

Metallic calcium. — Metallic calcium is prepared on a technical scale by the electrolysis of a mixture of 100 parts of calcium chloride and 16·5 parts of fluorspar, fused at 660° (or the pure chloride at 800°) in a bath formed of blocks of carbon. The cathode is an iron rod, which touches the surface of the fused chloride (Fig. 369). 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 readily sublimes in a vacuum below 800°. It exists in two forms with a transition point at 400° It is malleable, burns brightly in oxygen, combines with

sulphur, chlorine, nitrogen, etc., and reduces nearly all metallic oxides on heating.

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, 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 By heating calcium and calcium chloride in a steel cylinder at 1000°, red crystals of the **subchloride**, CaCl, are formed CaF and CaI are also known. Calcium reduces the chlorides and fluorides of alkali metals on heating, but not the iodides; when rapidly heated in carbon dioxide it forms CaO and CaC_2

By passing hydrogen or nitrogen over heated calcium, the **hydride**, CaH_2, and **nitride**, Ca_3N_2, respectively, are formed. On heating in ammonia, calcium forms the hydride and nitrogen 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 in the cold with formation of $Ca(NH_3)_6$ and evolution of heat. This compound ignites in air; in absence of air it forms $Ca(NH_2)_2$.

Calcium sulphate.—Calcium sulphate, $CaSO_4$, occurs as *anhydrite* along with limestone or rock-salt, or more commonly as the dihydrate *gypsum*, $CaSO_4,2H_2O$, which forms transparent crystals called *selenite* (often twinned), or 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°–90° 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.

Gypsum heated at 120°–130° 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 over 400°, slight decomposition into CaO and SO_3 occurs and *Estrich plaster*, which sets slowly and produces a smooth hard surface, used for floors, walls, etc., is formed.

Calcium sulphate begins to dissociate at 960°, when mixed with silica it reacts at 870°, and rapidly at 1280°. $CaSO_4 + SiO_2 = CaSiO_3 + SO_3$. Hydrogen chloride decomposes it at a red heat, forming $CaCl_2$.

Precipitated gypsum is formed by adding sulphuric acid to a solution of calcium chloride. It is used under the name of *pearl-hardening* for "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 $CaSO_4,2Na_2SO_4$, 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, $CaSO_3$, is formed as a white precipitate by passing sulphur dioxide through lime-water, or by adding a solution of a sulphite to one of calcium chloride. It dissolves in sulphurous acid, forming **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. On standing exposed to air it deposits crystals of $CaSO_3,2H_2O$.

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. 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.

Calcium sulphide, CaS, is formed as *alkali-waste* in the Leblanc process, or by heating gypsum with charcoal at 900°: $CaSO_4 + 4C = CaS + 4CO$, or in hydrogen at 600°–800°. Above 900°, CaS reacts with $CaSO_4$: $CaS + 3CaSO_4 = 4CaO + 4SO_2$.

Calcium sulphide is best prepared by passing hydrogen sulphide over heated slaked lime: $Ca(OH)_2 + H_2S = CaS + 2H_2O$. It is very sparingly soluble in water, but dissolves when hydrogen sulphide is passed through the suspension, forming the **hydrosulphide** which crystallises as $Ca(SH)_2,6H_2O$. The sulphide is hydrolysed by water: $2CaS + 2H_2O = Ca(OH)_2 + Ca(SH)_2$. The **polysulphides,** CaS_2 to CaS_5, or possibly CaS_7, appear to be contained in the reddish-yellow solution of sulphur in milk of lime (*thion hudor*). 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 heating the sulphite and sulphur with water If the solution is precipitated with sodium carbonate, sodium thiosulphate is formed : $CaS_2O_3 + Na_2CO_3 = CaCO_3 + Na_2S_2O_3$.

Calcium carbide.—Calcium carbide, CaC_2, was obtained by Wohler (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 in a closed electric furnace.

The furnace (Fig. 370) 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 over 2000°. 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 · $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$, 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. $CaC_2 + N_2 = CaCN_2 + C$ On heating barium carbide in nitrogen, barium cyanide, $Ba(CN)_2$, is formed

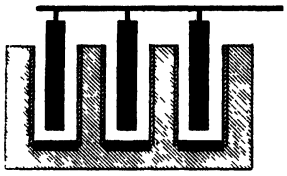


FIG 370.—Calcium carbide furnace

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.—This salt is present in the soil and serves as a plant food. It is manufactured by neutralising dilute nitric acid with limestone and evaporating, also by passing oxides of nitrogen into milk of lime, or a suspension of calcium carbonate in water, until the nitrite in the mixture is decomposed (p. 575). The salt forms very deliquescent monoclinic crystals, $Ca(NO_3)_2,4H_2O$, soluble in alcohol. According to T. W. Richards the best method of obtaining a pure calcium salt is repeated crystallisation of the nitrate from water or alcohol. The anhydrous salt dissolves in amyl alcohol.

Calcium phosphates.—Pure **calcium orthophosphate,** $Ca_3(PO_4)_2$, is not easy to obtain. It is formed as a white amorphous flocculent precipitate on adding ordinary sodium phosphate to a solution of

calcium chloride made alkaline with ammonia: $3Ca'' + 2HPO_4'' + 2OH' = Ca_3(PO_4)_2 + H_2O$. The purest product is obtained by precipitating with ammonium phosphate and a large excess of ammonia. 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**, $CaH_4(PO_4)_2,H_2O$, 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*, is prepared for use as a fertiliser by macerating ground mineral calcium phosphate in the form of phosphorites, etc, with two-thirds of its weight of sulphuric acid

$$5Ca_3(PO_4)_2 + 11H_2SO_4 = 4CaH_4(PO_4)_2 + 2H_3PO_4 + 11CaSO_4$$

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.

Calcium oxalate.—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 heating at 560° for 1 hour it gives the carbonate $CaC_2O_4 = CaCO_3 + CO$, or at a red heat the oxide, CaO. These reactions are used in the gravimetric estimation of calcium; in the volumetric method the precipitate of oxalate is washed, decomposed with warm dilute sulphuric acid, and the oxalate titrated at 60° 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 art of glazing a porous frit was developed very early in Egypt, and glass itself appears to have been known in the predynastic period (before 3400 B.C.), since pale green glass beads have been found in graves. In the period 2000–1500 B.C. an important glass industry developed in Egypt; a complete glass factory of about 1370 B.C. was excavated at Tell-el-Amarna by Sir Flinders Petrie. There is a blue glass bottle of Thothmes III. (1550 B.C.), and some other early Egyptian

glass, in the British Museum. The alkali (*natron*; sodium carbonate found in Egyptian lakes near Alexandria) was melted with sand or crushed quartz, copper compounds and perhaps limestone in crucibles to form a blue glass Red, yellow and milky white glasses were produced and nearly colourless glass was also made in an early period in Egypt. In the later period the Egyptian glass industry was established at Alexandria, from whence glass was exported to all parts of the Roman Empire, although in some places there were native glass factories, *e g*, in Syria and probably also in Britain, where remains of glass furnaces of the Roman period have been found near Warrington.

Glass making was also developed in Assyria. There is a glass bottle of King Sargon (700 B.C.) in the British Museum, where there are also some cuneiform tablets of about 650 B.C. describing the manufacture of coloured glass, particularly a blue glass called *uknu*, imitating lapis lazali.

The Egyptian glass industry was later introduced into Rome, Constantinople and Venice. The rest of Europe learnt the art from Venice.

Common glass contains calcium and sodium silicates, and has approximately the composition $Na_2O,CaO,5SiO_2$. On fusing silica with sodium carbonate a glassy mass of sodium silicate is formed on cooling, but this is soluble in water:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

Calcium carbonate is similarly decomposed but the calcium silicate, although glassy and insoluble in water, is soluble in acids:

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2.$$

Glass made by fusing together silica, calcium carbonate and sodium carbonate is transparent and insoluble both in water and in acids. Common *soda glass* is made by fusing 100 parts of sand, 35–40 of soda-ash (Na_2CO_3) and 15 parts of limestone, in fireclay pots or tanks at about 1375° C. or higher. A mixture of saltcake (Na_2SO_4) and charcoal may be used instead of soda-ash, when sulphur dioxide is evolved: $2Na_2SO_4 + C + 2SiO_2 = 2Na_2SiO_3 + CO_2 + 2SO_2$.

Ordinary glass always contains a small amount of aluminium oxide, perhaps derived from the crucibles. The sand used must be white and free from iron compounds for the best glass; crushed quartz and broken flints are also used.

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 a variety of potash-glass with lime 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. *Jena resistance*

glass has a low alkali content and a higher alumina content (which confers toughness) than ordinary glass, and contains barium and zinc oxides, and boron trioxide in place of some silica. *Pyrex glass*, resistant to heat and shock, is very rich in silica, poor in alkali and alumina, and contains boron trioxide. If glass is heated to its softening point some of the constituents slowly crystallise and the glass becomes opaque (*devitrification*). All varieties of glass require *annealing* before use: the objects are heated and allowed to cool slowly. Toughened glass is obtained by cooling in oil.

Optical glasses for lenses often contain special constituents such as boron trioxide and phosphorus pentoxide in place of silica, barium oxide in place of lime, and sometimes zinc oxide. Two main divisions of optical glasses are recognised: *crown glass*, containing as basic oxide mainly potash or barium oxide; and *flint glass*, containing lead oxide. By combining lenses of these two types, dispersion is eliminated. *Crookes's glass*, for spectacles, contains rare earth compounds (praseodymium and neodymium): it allows visible light to pass but absorbs the ultra-violet. A glass containing nickel, on the contrary, which is very dark red, absorbs nearly all the visible light but allows a part of the ultra-violet spectrum to pass through. Ordinary glass absorbs the infra-red rays (radiant heat), hence its use for glass firescreens.

Coloured glasses are made by adding various metallic compounds 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 present:

Ruby gold, selenium, or cuprous oxide.
Green: chromic oxide, or cupric oxide with chromic or ferric oxides and a reducing agent.
Yellow. carbon and sulphates in the melt, cadmium sulphide, sometimes uranium or selenium.
Violet: manganese dioxide.
Blue: cobalt oxide.
Opaque milky glass fluorspar with felspar; cryolite; sometimes tin oxide or calcium phosphate.
Fluorescent greenish-yellow glass. uranium oxide.
Black glass: large quantities of ferric oxide and cupric oxide, or cobalt, nickel and manganese oxides

Strontium and Barium.

Strontium and barium minerals.—The mineral *heavy spar* or *barytes* (Greek *barus* = 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, Vincenzo Cascariolo, 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 *barote* by Guyton de Morveau and *barytes* by Kirwan. The metals barium and strontium were obtained by Davy in 1808. Barium also occurs as the carbonate, $BaCO_3$, the mineral *witherite*, isomorphous with aragonite and a gangue material in lead veins. *Alstonite*, $BaCO_3,CaCO_3$, rhombic, and *barytocalcite*, a monoclinic form, also occur as minerals.

A peculiar mineral found in the lead mine of Strontian in Argyllshire was examined by Hope in 1791, by Kirwan and by Klaproth in 1793. They concluded that it was the carbonate of a new earth, different from lime and baryta, which Hope called *strontites* and 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.—The native carbonates are dissolved in hydrochloric acid, the iron in the solutions is oxidised with chlorine water, and precipitated by boiling with a little of the strontium or barium carbonates obtained by adding sodium carbonate to a portion of the solution The filtered liquid is evaporated, and 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. Anhydrous strontium chloride is sparingly soluble in alcohol, which will, however, dissolve it from admixture with the almost insoluble barium chloride, which is moderately soluble in methyl alcohol. The bromides and iodides are readily soluble in alcohol. A **barium subchloride**, BaCl, is formed by heating barium and barium chloride in a vacuum at 850°, or at the cathode by the electrolysis of fused or solid $BaCl_2$. It decomposes water, with evolution of hydrogen.

By dissolving the carbonates in dilute nitric acid, **strontium nitrate**, $Sr(NO_3)_2$, and **barium nitrate**, $Ba(NO_3)_2$, are formed. These salts are used in pyrotechny mixed with sulphur and charcoal to produce *crimson* and *green fire*, respectively. Strontium or barium salts are freed from calcium by precipitating solutions of the nitrates with alcohol, in which calcium nitrate is soluble. Barium nitrate is less soluble in water than strontium nitrate; it is precipitated from saturated barium chloride solution by nitric acid. Strontium nitrate is less soluble than calcium nitrate. A pure barium compound is best obtained by repeated crystallisation of the nitrate, and then precipitating barium carbonate with ammonium carbonate; strontium nitrate is freed from barium by adding calcium sulphate solution to the nitrate, filtering, and crystallising.

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 excess of 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 Barium sulphate requires a high temperature for reduction The carbonates or sulphides may then be dissolved in acids, and the salts crystallised. **Barium sulphide**, BaS, is best obtained by the action of H_2S on $Ba(OH)_2,H_2O$ at 200°. It is easily soluble and is hydrolysed $2BaS + 2H_2O \rightleftharpoons Ba(OH)_2 + Ba(SH)_2$. Polysulphides of barium and strontium are known.

Strontium carbonate is decomposed at a higher temperature than calcium carbonate (*c.* 1 atm at 1155°), whilst **barium carbonate** is stable at a bright red heat The dissociation pressures ($BaCO_3 \rightleftharpoons BaO + CO_2$) are:

$t°$ C -	- 915	1020	1120	1220	1300	*c* 1352
p mm -	- 0 4	4·3	24·4	114	381	760

Barium carbonate attacks platinum at a red heat. When undecomposed it does not melt at 1350°, but in presence of oxide it fuses below 950°. If the carbonates of barium or strontium are mixed with charcoal and heated to redness, the **oxides** are more readily formed: $BaCO_3 + C = BaO + 2CO$ Barium carbonate heated in steam gives the hydroxide and carbon dioxide.

The solubilities of strontium and barium carbonates are 0·010 and 0·021 gm per litre at 15°, respectively. Barium carbonate is slightly hydrolysed a suspension of it precipitates ferric, chromic and aluminium hydroxides from the salts, but not zinc or manganese.

The oxides are best prepared by heating the nitrates (strongly in the case of barium nitrate, otherwise the peroxide is formed) Barium oxide is obtained pure by heating barium iodate. They are white when pure, amorphous, resembling quicklime, but more fusible, 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 the oxide, 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 $Ba(OH)_2,H_2O$, and at 100°, $Ba(OH)_2$ is formed. Barium hydroxide fuses on heating, but does not lose water completely even at a very high temperature. Strontium hydroxide $Sr(OH)_2,8H_2O$ effloresces to $Sr(OH)_2,H_2O$, which at 100° forms $Sr(OH)_2$ The latter forms SrO at 700°. A solution of barium hydroxide in water is called baryta-water and gives a white precipitate of the carbonate, $BaCO_3$, with carbon dioxide.

Barium hydroxide 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.

Baryta and strontia, as well as lime, form sparingly soluble compounds called **saccharates** with cane-sugar, *e.g.*, $C_{12}H_{22}O_{11},2SrO$; $C_{12}H_{22}O_{11}$, $3CaO$. The precipitates, suspended in water, are decomposed by a current of carbon dioxide. The carbonate is precipitated, pure sugar remains in solution, and may be crystallised. Barium salts are poisonous.

Barium peroxide, BaO_2, is obtained by passing dry oxygen or air free from carbon dioxide over baryta heated to dull redness: $2BaO + O_2 \rightleftharpoons 2BaO_2$. The dissociation pressures at different temperatures are:

555°	650°	720°	790°	795° C.
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 50°, anhydrous SrO_2 is formed, below 40° the compounds BaO_2,H_2O_2 (yellow) and $BaO_2,2H_2O_2$ are formed with excess of hydrogen peroxide and baryta-water

Metallic **strontium** and **barium** are obtained by heating the oxides with 10 per cent of peroxide and aluminium powder *in vacuo* They are silver-white and soft. Barium inflames spontaneously in air, and strontium is nearly as reactive. Barium is also obtained by heating the oxide with silicon in an evacuated steel tube $3BaO + Si = BaSiO_3 + 2Ba$. The metal distils off. Pure barium was obtained by Guntz by *slowly* distilling the amalgam obtained by electrolysis with a mercury cathode. It is volatile and distils over after the mercury. Strontium is freely volatile at 950°

Barium and strontium (or their amalgams) readily absorb hydrogen on heating at 1000°, forming **hydrides**, BaH_2 and SrH_2 By heating these strongly in a vacuum in an iron tube enclosed in a porcelain tube they decompose, and the pure metal may be condensed on a polished steel tube cooled by water When heated in nitrogen the metals form black **nitrides**, Ba_3N_2 and Sr_3N_2, decomposed by water with evolution of ammonia

Strontium sulphate, $SrSO_4$, dissolves to the extent of 1 gm. per litre of water at 15°. It is less soluble in dilute sulphuric acid and practically insoluble in alcohol, but is more soluble in salt solutions, including strontium salts (*e g.*, 1·987 gm. per litre in 10 per cent. $Sr(NO_3)_2$).

Barium sulphate, $BaSO_4$, is formed, by adding sulphuric acid or a sulphate to a barium salt, as a fine white precipitate nearly insoluble in water (2·4 mgm. per litre) and acids, except hot concentrated sulphuric acid which forms the **acid sulphate**, $Ba(HSO_4)_2$, or in hot very concentrated hydrochloric acid. It is used as a pigment (*permanent white*) but has a poor covering power. *Lithopone* is a mixture of

$BaSO_4$ and zinc sulphide and oxide made by precipitation: $BaS + ZnSO_4 = BaSO_4 + ZnS$, and heating the precipitate. It has a good covering power, does not darken on exposure to hydrogen sulphide, but darkens on exposure to light.

Barium sulphate carries down from solution various soluble salts, especially potassium sulphate and sulphates, salts of tervalent metals (Fe, Cr), nitrates, and chlorates, which cannot be removed by washing It also adsorbs barium chloride and is slightly soluble in dilute hydrochloric acid and in many salt solutions Barium sulphate is only slightly decomposed at 1300°, it melts at 1580° and decomposes at 1600°. These properties are of importance in quantitative analysis. Barium and strontium sulphates are converted into carbonates by boiling with alkali carbonate, and the reaction is reversible Barium sulphate is almost quantitatively converted to carbonate on fusion with 8–9 mols of K_2CO_3, but barium carbonate is only very incompletely converted into sulphate on fusion with K_2SO_4

Strontium phosphate, $Sr_3(PO_4)_2$, is an amorphous solid precipitated from neutral solution by Na_3PO_4. The precipitate of $SrHPO_4$ formed with Na_2HPO_4 is at first amorphous, but then crystallises On heating it forms $Sr_2P_2O_7$, the pyrophosphate, and the metaphosphate, $Sr(PO_3)_2$, is also known No $Sr(H_2PO_4)_2$ is known, but the corresponding barium compound has been prepared.

CHAPTER XLII

THE METALS OF THE ZINC GROUP

Beryllium.—Vauquelin, in 1798, found that the mineral *beryl* (Fig. 371) contains a peculiar earth, which was called glucina, differing from lime and alumina by forming a soluble sulphate which does not produce alums The true, or Peruvian, *emerald* (*cf* p 877) is a transparent variety of beryl, coloured green by oxide of chromium *Aquamarine* is a bluish-green variety. The formula of beryl is $3BeO,Al_2O_3,6SiO_2$

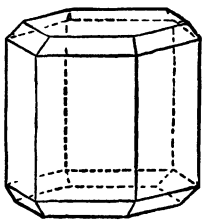


FIG 371.—Crystal of beryl

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 and allowed to stand **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**, 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* formerly 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 (b pt. 520°) corresponds above 630° with the formula $BeCl_2$. 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. 1350°, which burns brilliantly in the air when heated in the form of powder, but does not decompose steam even at a red heat. It is readily soluble in hydrochloric acid and in dilute sulphuric acid, but not in nitric acid, and readily

soluble in alkalies (*cf* aluminium). Beryllium is a constituent of some light alloys

Beryllium hydroxide, $Be(OH)_2$, is soluble in alkalies, but is reprecipitated on boiling the solution It is readily soluble in ammonium carbonate and a basic carbonate is precipitated on boiling the solution or passing a rapid current of steam through it. By these reactions it is distinguished from alumina, which it otherwise closely resembles. **Beryllium nitrate,** $Be(NO_3)_2$, is used in making gas mantles, a small quantity being added to the thorium and cerium nitrates (p. 912). In Group II beryllium resembles zinc most nearly

On evaporating beryllium hydroxide with acetic acid, a characteristic **basic acetate,** $Be_4O(C_2H_3O_2)_6$, is formed This is readily volatile (b pt 330°), giving the normal vapour density and is soluble in chloroform. The X-ray examination of the crystalline compound shows that the four beryllium atoms are arranged at the corners of a regular tetrahedron, with the oxygen at the centre, and the six edges are occupied by the acetate groups.

MAGNESIUM.

Magnesium.—In 1695 Nehemiah Grew obtained from the water of a mineral spring at Epsom a peculiar salt which was called *Epsom salt.* The salt was afterwards found in other mineral springs, in the mother liquors from the preparation of common salt from seawater, and in saltpetre mother liquors. Epsom salt is **magnesium sulphate,** $MgSO_4,7H_2O$; **magnesium chloride,** $MgCl_2$, is contained in seawater. By precipitating solutions of these salts with potassium or sodium carbonate, a basic carbonate called *magnesia alba,* which like Epsom salt is used medicinally, is obtained. Black in 1754 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 in 1808.

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* 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.

Magnesium sulphate.—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 sulphate, 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 (Fig. 372) of magnesium sulphate $MgSO_4$, $7H_2O$ (*Epsom salt*). 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

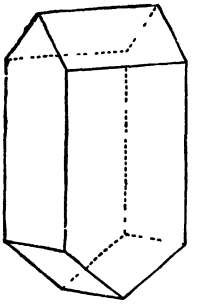


FIG. 372.—Epsom salt crystal

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 common hydrate $MgSO_4,7H_2O$ is isomorphous with $ZnSO_4,7H_2O$. A monoclinic variety, isomorphous with $FeSO_4,7H_2O$, is known Double salts with alkali-metals are readily formed, *e g*, $MgSO_4,K_2SO_4$, $6H_2O$ is *schonite*, a Stassfurt mineral A solution of the anhydrous sulphate in concentrated sulphuric acid deposits crystals of $MgSO_4,H_2SO_4$ When very strongly heated in air, magnesium sulphate decomposes, leaving the oxide

The **double salts** in solution are almost 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 $K_4Fe(CN)_6 \rightleftharpoons 4K + Fe(CN)_6''''$. The solution then does not exhibit the reactions of the components of the complex ion (*e.g.*, $Fe^{..}$ 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 formulae as $(Fe,Mg)SO_4,7H_2O$

Magnesium chloride.—Carnallite, $KCl,MgCl_2,6H_2O$, occurs in large quantities in the Stassfurt deposits. 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 chloride 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 an **oxychloride**, Mg_2OCl_2, is left: on strongly heating in air this evolves chlorine and leaves the oxide. 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 platinum dish inside a large clay crucible. The double salt $MgCl_2,NH_4Cl,6H_2O$, which is left on evaporation, loses water and the residual $MgCl_2.NH_4Cl$ on further ignition evolves hydrogen chloride and ammonia, leaving fused anhydrous magnesium chloride (m pt. 718°).

The hydrolysis at higher temperatures 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**, $MgBr_2,6H_2O$, 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. The **fluoride**, MgF_2, is sparingly soluble

If a concentrated solution of magnesium chloride is mixed with magnesium oxide, the paste solidifies to a hard, white mass of an **oxychloride** ($MgCl_2,5MgO,17H_2O$?). 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 then fuses to a clear liquid below 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 electrolysis of magnesium oxide dissolved in molten magnesium fluoride is also used. The semi-fused metal is pressed into wire, which is then rolled into ribbon.

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. It also continues to burn in sulphur vapour, steam, carbon dioxide, sulphur dioxide, nitric oxide and nitrogen dioxide ; it reduces carbon monoxide when heated. Magnesium reduces sodium and potassium oxides on heating. Magnesium powder mixed with powdered potassium chlorate or barium peroxide burns explosively when ignited, 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 may also be 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 1380°. It is very light (sp. gr. 1·74). Light alloys containing magnesium are used, *e.g.*, *elektron* is 95 Mg and 5Zn; some copper, aluminium and cadmium may be present. 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 hot water. A colloidal solution in ether can be prepared by Bredig's method.

Magnesium combines directly with nitrogen on strong heating, forming a greenish-yellow amorphous nitride, Mg_3N_2, decomposed by water: $Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$ It is more easily obtained by heating magnesium in ammonia gas 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, so that alkali sulphides precipitate only the hydroxide, but a solution probably containing the **hydrosulphide**, $Mg(HS)_2$, is formed by passing hydrogen sulphide 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, evolving PH_3 and AsH_3, respectively.

Magnesia.—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 2800°, 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 (chrome-ironstone). Bricks containing 90 parts of MgO, 5 of FeO, and 5 of silica, lime and alumina, sinter above 1400°, but do not fuse below 2000°.

The solubility of magnesium hydroxide (0·1 gm. per litre of water) is reduced by the addition of potash or soda, in accordance with the equation $Mg(OH)_2 \rightleftharpoons Mg^{\cdot} + 2OH'$, 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. Magnesium salts are scarcely hydrolysed, magnesia is a strong base.

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 hydrate $MgCO_3,3H_2O$ is the rare mineral *nesquehonite*. This also crystallises after 3 days from a solution of 20 gm. of Epsom salt and 14 gm. of sodium bicarbonate in 150 c.c. of water. The precipitates formed by adding carbonates to solutions of magnesium salts are always **basic carbonates**. From solutions at the ordinary temperature, the precipitate after drying is a light loose powder—*magnesia alba levis*, of variable composition, $xMgCO_3 + yMg(OH)_2 + zH_2O$. From a boiling saturated solution, a denser crystalline precipitate is thrown down, this is evaporated to dryness, washed, and dried at 100°, and is known as *magnesia alba ponderosa*. 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 12 gm. of $Mg(HCO_3)_2$ per 100 c c. is known as *fluid magnesia*. If the solution is heated to 50°, crystals of $MgCO_3,3H_2O$ separate. Magnesium carbonate is formed by the action of magnesium chloride on calcium carbonate and is then not easily soluble in dilute acids. A second form, which "sets" with water, is obtained by heating magnesium ammonium carbonate. The crystalline carbonate dissociates so as to give 760 mm. pressure of CO_2 at 445°.

Magnesium phosphate.—The tertiary phosphate, $Mg_3(PO_4)_2$, occurs in bones and in the seeds of cereals, and is precipitated from solutions of magnesium salts by trisodium phosphate, Na_3PO_4. Ordinary sodium phosphate, Na_2HPO_4, slowly precipitates **magnesium hydrogen phosphate**, $MgHPO_4,7H_2O$, 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 $MgH_4(PO)_2$, 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 of 1 vol. conc. ammonia + 1 vol. water); its formation is a test for a phosphate or magnesium On heating to dull redness 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 nitrate.—This salt is prepared by dissolving the oxide or carbonate in dilute nitric acid. It separates from solutions at the ordinary temperature in deliquescent crystals, $Mg(NO_3)_2,6H_2O$.

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 $MgNH_4PO_4$.

Zinc, Cadmium and Mercury.

	Zn	Cd	Hg.
Atomic number	30	48	80
Electron configuration	2 8·18·2	2·8·18·18·2	2·8·18·32·18·2
Density	7·1	8·64	13·55
Atomic volume	9 21	13 01	14 81
Melting point	419 4°	320·9°	−38·87°
Boiling point	907°	767 3°	356·9°

Zinc.

Zinc minerals.—Plato (400 B C.) refers to *orichalcum*, probably *brass*, an alloy of zinc and copper no doubt obtained by heating copper with an ore known as *cadmia* and charcoal. Brass of the period 1500 B.C., containing 23 per cent. of zinc and 10 per cent of tin, was found at Gezer in Palestine. Cadmia, which was called *tutia* or *tutty* by the alchemists, was probably zinc carbonate, $ZnCO_3$, or oxide, ZnO. The name is said to occur as *tusku* in Assyrian tablets of 650 B.C Deposits of calamine, native zinc carbonate, occur in the old silver mines of Laurion, in Greece. Strabo (60–20 B.C.) describes the preparation of the metal, which he calls "mock-silver," by heating the oxide with coal. A statuette from Thrace of about his time consists of zinc with 11·5 per cent. of lead and a little iron. Since copper was turned a golden-yellow colour in making brass, tutia was looked upon as an approach to the Philosopher's Stone. 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 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 a peculiar kind of tin called *calaen*, brought from the East Indies. The extraction of zinc seems to have been carried out at an early period in China. 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 Isaac Lawson in 1730, and in 1743 the first European zinc works was started by John Champion at Bristol.

Zinc occurs 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, in Rhodesia, Burma, and New South Wales The carbonate occurs as *calamine* or *smithsonite*, $ZnCO_3$. *Electric calamine* is a silicate, Zn_2SiO_4,H_2O. The anhydrous silicate is *willemite*. The oxide, *zincite*, ZnO, or *red zinc ore*, is rare, but the ferrite, $Zn(FeO_2)_2$, or ZnO,Fe_2O_3, forms the important *franklinite* 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 in snake venom (0·11–0·56 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 907°) 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 blende being raked in a series of muffles through which air circulates, or on a furnace hearth. Care must be taken that only the oxide is produced: $2ZnS + 3O_2 = 2ZnO + 2SO_2$, since the sulphate, $ZnSO_4$, is very stable and would in the subsequent reduction again give sulphide, leading to considerable

loss. Some sulphate which is always formed is decomposed at the high temperature used. 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 An iron tube is luted into the open end with clay and serves to condense the zinc. The Silesian retorts are fireclay muffles, to which a fireclay and an iron condenser tube are luted, they are heated in a furnace (Fig. 373). The

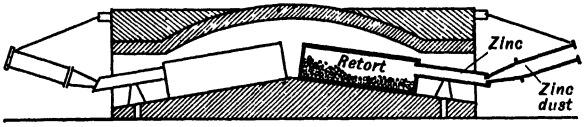


FIG 373 —Technical preparation of zinc.

newer Belgo-Silesian 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, about half in the ash and half as vapour.

The oxide 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 fuel-fired furnaces

Commercial zinc, called *spelter*, contains about 97–98 per cent. of zinc, 1–3 per cent. of lead, up to 0·1 per cent. of iron, more rarely cadmium and some arsenic. It is refined by electrolysis in an acid solution of zinc sulphate with a high current density (Pring and Tainton).

The deposition voltage of zinc is 0·785, *i e*, higher than the *reversible* deposition voltage of hydrogen But the overvoltage of hydrogen on zinc is large (1·23 volts in *N* acid), hence zinc deposits and not hydrogen The electrolyte must be very pure so called " chemically pure " zinc salts are not good enough Antimony and cobalt are very prejudicial. 1 part per million of antimony affects the result. The effect of cobalt may be counteracted by adding glue. The voltage is 3·25–3·5, the current density is 20–30 amp per sq. ft, lead anodes and pure aluminium cathodes being used. The best grade of zinc should not contain more than 0·005 per cent. iron and 0·05 per cent. lead; the cadmium content depends on the purity of the solution but the metal is usually 99·9 per cent. zinc. The zinc is stripped from the cathodes, the deposit is bright with 2–3 per cent. of free acid and the bath is not allowed to run above 0·66 *N* acid.

Zinc is also produced directly from blende by roasting below 650° to oxide (and a little sulphate), leaching with dilute sulphuric acid and spent electrolyte, precipitating Fe, Al, As, Sb and SiO_2 by milk of lime, and Cu and Cd by zinc dust (excess is required to precipitate all the cadmium, which is recovered). The liquid is filtered in vacuum filters and goes to the electrolytic cells, some spent acid electrolyte being added.

Zinc dust is made by atomising molten zinc with a blast of air, and consists of small spheres of zinc coated with oxide. It always contains oxide, but the good kinds may contain over 90 per cent of metallic zinc. Zinc nitride may be present Zinc oxide may be removed by washing with very dilute hydrochloric acid, water and alcohol, and drying

Ordinary zinc dissolves readily in dilute acid, whereas some varieties of the very 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. Grove (1839) found that the amalgamated metal is not attacked by acids; the commercial varieties are more resistant when amalgamated than the amalgamated pure metal (J. N. Friend, 1929). 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 crystallises in hexagonal prisms, has a bluish-white colour, melts at 419·4°, and boils at 907°. Its vapour density corresponds with the formula Zn. The metal is moderately hard and 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 into *nihilum album*. The metal oxidises in moist air, forming a greyish-white crust of the basic carbonate, and is attacked and dissolved by soft water, especially that containing peat acids, or sea-water. The zinco-solvency of fresh water is reduced by allowing it to stand over limestone.

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 dissolves to a limited extent only in lead and bismuth.

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 spraying or by heating them in zinc dust (*sherardising*). The zinc dissolves before iron in presence of oxygen and moisture, since it has

a higher solution pressure than iron (p. 865). The metal is also used for the negative electrodes of voltaic cells.

Zinc dissolves in dilute acids, evolving hydrogen (except with nitric acid) and producing zinc salts (p. 150) containing the cation $Zn^{\cdot\cdot}$. It also dissolves readily in hot solutions of caustic potash and soda, evolving hydrogen and forming solutions of **zincates**, containing the anion ZnO_2'' : $Zn + 2KOH = K_2ZnO_2 + H_2$.

Brass.—Copper and zinc form two definite compounds Cu_2Zn_3 and (probably) CuZn, and also two types of solid solutions called α- and β-brass The alloys (*brasses*) are of two main types (1) those with more than 64 per cent. of copper, which are homogeneous α-solution ; (2) those with 55–64 per cent. copper, composed of α- and β-solutions. Brasses of 70 copper + 30 zinc typify (1) and those of 60 copper + 40 zinc typify (2).

The effect of adding zinc to copper is to increase progressively the strength, toughness and hardness of the alloy up to 36 per cent. zinc, after which the increase in strength is more marked. Various alloys containing from 2 to 36 per cent. of zinc are made.

Gilding metal (3–8Zn), *tombac* (gold colour : 10–18Zn), *pinchbeck* (dark gold colour, 7–11Zn) are low in zinc. *Cartridge brass* is 70Cu + 30Zn, *common brass* for sheets is 2Cu to 1Zn. All α-brasses are ductile and can be worked cold . tin, lead and aluminium are often added for special purposes, *e g.*, for condenser tubes the alloy contains 29Zn and 1Sn The usual *casting brass* contains 27Zn, 2Pb and 1 Sn. *Muntz metal* contains 60–62 Cu and 40–38 Zn. Brass with 1·5 to 2 per cent. of lead machines better ; for free turning qualities 2 to 3 per cent. may be present. Manganese is added to 60 40 brass to increase the strength but often only traces are present in *manganese bronze* A brass containing 2 per cent. of manganese takes a dark brown or chocolate colour when extruded hot, due to a film of oxide, and is used for window-frames. *Arch metal* is 60Cu, 2Fe, and 38Zn ; *Sterro metal* contains more iron. High tensile brasses contain nickel in place of copper, *e g* , 50Cu, 45Zn and 5Ni. If the zinc is kept at 45, the tensile strength increases up to 12 per cent Ni. Alloys with 45 each of copper and zinc and 10 of nickel are white (*nickel brasses*) and can be worked hot.

Zinc oxide.—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 heating the basic carbonate. It is a white powder which becomes sulphur-yellow on heating, the colour disappearing on cooling. A crystalline oxide is formed by the action of steam on zinc at a red heat. Zinc oxide sublimes appreciably at 1400°. It is reduced by hydrogen above 450°. 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.*, $Na_2ZnO_2,4H_2O$, 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. Crystals are obtained by allowing a zinc plate and iron turnings to stand in concentrated ammonia It can be dried at 85° but loses water at higher temperatures. Zinc hydroxide dissolves in 190,000 parts of water at 18°. The precipitate is readily soluble in excess of the alkali, producing a solution containing colloidal zinc hydroxide and zincate. Zinc hydroxide is therefore feebly acidic as well as basic; it is an amphoteric substance (p. 523) Ammonia also dissolves it, forming a complex hydroxide: $Zn(NH_3)_4(OH)_2 \rightleftharpoons Zn(NH_3)_4^{\cdot\cdot} + 2OH'$.

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 cobalt zincate, $CoZnO_2$, in solid solution in zinc oxide. The formation of this green substance is the basis of the blowpipe test for zinc.

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 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 chloride.—Anhydrous zinc chloride is a soft white mass (b. pt. 730°), subliming at a red heat in white needles, formed by passing hydrogen chloride over heated zinc or by distilling the metal with mercuric chloride: $HgCl_2 + Zn = Hg + ZnCl_2$. Chlorine decomposes zinc oxide at 700°, forming the chloride with evolution of oxygen. 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 of $ZnCl_2,H_2O$ separate. If the aqueous solution is evaporated to dryness, the **oxychlorides** Zn(OH)Cl and Zn_2OCl_2, are formed to some extent, but if the dry mass is distilled at a red heat the anhydrous chloride passes over. By evaporation in a current of hydrochloric acid gas the fused salt is obtained, and may be cast into sticks. It is very deliquescent and is soluble in alcohol, ether, acetone and pyridine. 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.

A solution of zinc chloride prepared by adding zinc to commercial hydrochloric acid (spirit of salt) is used under the name of "killed spirit" 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 was used to form the carbon filament of the old type electric lamps Zinc chloride is used, like magnesium chloride, for "filling" (*i e.*, weighting) cotton goods. The salt $ZnCl_2,2NH_3$ is formed as crystals in Leclanché batteries, and zinc chloride absorbs ammonia gas to form a number of compounds, *e g*, $ZnCl_2,4NH_3$ These 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 The **fluoride**, $ZnF_2,4H_2O$, is sparingly soluble

Zinc sulphate.—Zinc sulphate, $ZnSO_4,7H_2O$, isomorphous with Epsom salt, is known as *white vitriol.* It was described by Basil Valentine (p. 27), and was produced by lixiviating roasted blende. Its composition was correctly given by Neumann (1735). The sulphate is the commonest salt of zinc and is prepared by dissolving the metal, oxide or carbonate in dilute sulphuric acid evaporating, and crystallising below 30°. Above 30°, $ZnSO_4,6H_2O$ is deposited. On heating $ZnSO_4,7H_2O$ at 100°, $ZnSO_4,H_2O$ is left, which loses water only at 450°. When strongly heated, sulphur trioxide is evolved and a basic salt, or at a higher temperature, zinc oxide, remains. It is said that zinc sulphate is completely decomposed to the oxide at 767°. Double salts, *e g.*, $K_2SO_4,ZnSO_4,6H_2O$, are easily prepared. A solution of white vitriol ($\frac{1}{2}$ per cent. $ZnSO_4$) is used as an eye lotion, and the sulphate is used in the manufacture of lithopone (p. 832).

Zinc sulphide.—Zinc sulphide, ZnS, occurs as *blende* in regular crystals, and more rarely as *wurtzite* in hexagonal crystals. Wurtzite may be formed from zinc vapour and hydrogen sulphide. An artificial phosphorescent sulphide (*Sidot's blende*) formed on heating the precipitated sulphide to whiteness in a covered crucible, is used in making phosphorescent screens for X-ray and radio-activity work. Perfectly pure zinc sulphide is not phosphorescent; the property is conferred by traces of alkali chlorides and sulphides of heavy metals (bismuth, copper, manganese). Massive zinc and sulphur do not react easily on heating, but the powders react with incandescence and the mixture may detonate on percussion. The sulphide is easily obtained by heating zinc oxide with sulphur. Zinc sulphide is obtained as a white precipitate on adding ammonium sulphide to a solution of a zinc salt; it is insoluble in excess of reagent but dissolves in all dilute mineral acids, but not in acetic acid (*cf.* MnS). If

hydrogen sulphide 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.

Phosphorescence.—Reference has been made to the phosphorescence of calcium sulphide and nitrate, and of barium and zinc sulphides, *i e.*, the property which these materials possess of shining after exposure to light, especially sunlight. This is utilised in the preparation of *luminous paint*. Pure compounds do not exhibit phosphorescence; the property 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 (all weights in grams)

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.

5 *Golden yellow light* (unusual): $BaCO_3$ 25, $Sr(OH)_2$ 15, S 10, starch 3, Li_2SO_4 1, MgO 1, $Th(SO_4)_2$ 2 c c of 0·5 per cent solution, $CuSO_4$ 3 c c of 0·4 per cent solution. Heat 40 minutes

Zinc carbonate.—Sodium carbonate precipitates a white **basic carbonate** from a solution of a zinc salt, the composition depending on the concentrations and temperature. A solution of an alkali bicarbonate gives a white precipitate of **zinc carbonate,** $ZnCO_3$, soluble in a concentrated solution of potassium carbonate, but precipitated on dilution. A crystalline carbonate is formed by heating a solution of the sulphate with sodium bicarbonate in a sealed tube at 160°. When boiled with sodium carbonate solution the carbonate or basic carbonates form zinc oxide. Zinc, or zinc oxide, dissolves in water containing carbon dioxide.

Zinc cyanide, $Zn(CN)_2$, is formed 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

Zinc amide, $Zn(NH_2)_2$, is formed by the action of ammonia on zinc ethyl (*q.v.*) in dry ether · $Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6$. On heating to dull redness it forms the **nitride**, Zn_3N_2, a grey or green powder vigorously decomposed by water $3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3$; $Zn_3N_2 + 3H_2O = 3ZnO + 2NH_3$ 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 . $2Zn(C_2H_5)I = Zn(C_2H_5)_2 + ZnI_2$.

Zinc phosphate, $Zn_3(PO_4)_2,4H_2O$, is obtained by heating a solution of zinc sulphate and Na_2HPO_4 in the form of pearly scales, insoluble in water and dilute acids. On heating it forms the infusible anhydrous salt.

Complex ammine 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.

Estimation of zinc —Zinc is estimated by precipitation as basic carbonate, ignition, and weighing as ZnO, by precipitation of $ZnNH_4PO_4$ and ignition to $Zn_2P_2O_7$, or by electrolysis of an alkaline solution In the volumetric method it may be titrated with potassium ferrocyanide standardised with a known zinc solution, uranium acetate being used as outside indicator . excess of ferrocyanide then gives a brown colour with the uranium salt

Cadmium.

Cadmium.—Most zinc ores contain small amounts of 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., but the average is less than 0·5 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 ore (καδμεία, in Dioskorides). 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. The salts are poisonous.

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. or more 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 In America much cadmium is extracted from the fumes from lead and copper furnaces, and some from the vat residues in electrolytic zinc refining, from which it is precipitated by zinc (p. 843).

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. 71°, consists of 4 parts of bismuth, 2 of lead, 1 of tin, and 1 of cadmium Cadmium is a soft bluish-white metal, sp. gr. 8·64, melting at 321° and boiling at 767°. 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°. On bending, it " rustles " like tin. It is slowly oxidised in air, forming a protective coating, and very thin deposits (0·0002 in.) of plating are used to protect iron and steel from rust. They may be heat treated to form an alloy with the iron.

Cadmium (1 per cent.) is alloyed with copper for overhead tramway wires, is added (0·5–5 per cent) to aluminium for casting, and is also added to silver to decrease staining. It is used in antifriction alloys and in solders in place of tin.

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 in minute crystals by adding excess of ammonium carbonate to a solution of cadmium chloride, then just enough ammonia to dissolve the precipitate, and heating on the water bath The white precipitate thrown down by alkali carbonates from solutions of cadmium salts is of variable composition, as in the case of zinc. On heating the hydroxide or carbonate, or by burning the metal in air, the oxide CdO is formed.

Of the soluble salts of cadmium, the **sulphate**, $3CdSO_4,8H_2O$, and the **chloride**, $2CdCl_2,5H_2O$, which is efflorescent and is not hydrolysed by water (*cf.* $ZnCl_2$), are most important. The peculiar formulae of the crystalline salts are noteworthy. The halogen salts are all soluble

in water but are only very feebly ionised in solution, forming complex ions in which the metal exists in the negative ion: $2CdI_2 \rightleftharpoons Cd\,CdI_4 \rightleftharpoons Cd^{\cdot\cdot} + CdI_4''$. 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 salt and the solubility product of the sulphide etc 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 hydrogen sulphide through a solution of a cadmium salt which is not too strongly acid. In more acid solutions a *red* form is precipitated—perhaps only because the particles are larger. If the acid concentration exceeds 1·3 normal the sulphide is not precipitated: $H_2S + CdSO_4 \rightleftharpoons CdS + H_2SO_4$. According to Treadwell, a double salt is always present in the precipitate, *e.g.*, Cd_2Cl_2S.

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 (p. 797)

Cadmium dissolves in fused cadmium chloride and on treating with water a white precipitate of **cadmous hydroxide**, CdOH, is formed. (The solid probably contains CdCl) On gently heating this, yellow **cadmous oxide**, Cd_2O, is obtained A green form of Cd_2O is obtained by heating cadmium oxalate and distilling off the cadmium in a vacuum (Denham.)

Mercury.

Mercury.—Metallic mercury, which is peculiar in being liquid at the ordinary temperature, is first mentioned by Aristotle (350 B.C.); both he and Theophrastos (300 B.C.) refer to it as *liquid silver* (*chutos argyros*); Dioscorides (*c.* 50 A.D.) calls it *hydrargyros*. Pliny speaks of native mercury as quicksilver · *argentum vivum*, and the metal obtained by heating *cinnabar*, HgS, its important ore, as *hydrargyrum* (liquid silver). The metal, he says, 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. By convenient *Preparation* 'tis possible to take away such Impurity and supply the *Deficiency* in Perfect Bodies." Compounds of mercury, including 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.

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. $-38{\cdot}9°$) by Braune in 1759, although the freezing of mercury in a thermometer was noticed in Siberia in 1736. 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 or black mineral found in Almaden (Spain), Idria, Monte Amiata (Italy), and in smaller amounts in Peru, California, Mexico, China, and Japan. Pliny says that 10,000 lb. of cinnabar (*minium*) came annually from Spain in his day. 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. 374). The ore rests on a perforated arch,

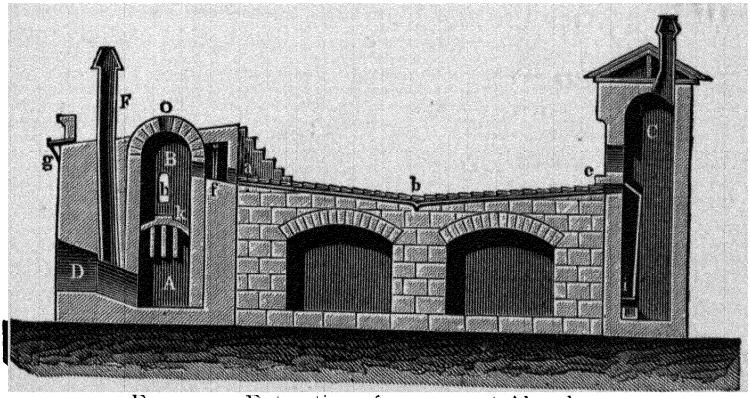


FIG. 374.—Extraction of mercury at Almaden.

k, heated below by a fire, *A*. Air enters through *D*, and the vapours pass through six openings, *f*, into series of stoneware aludels, 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, holding about 75 lb. Ten of these *Bustamente furnaces* were built at Almaden in 1646–54 and all are still in use.

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 *Cermak-Spirek* furnace is used at Almaden, Monte Amiata and Idria; in America rotary furnaces or *Scott tile and stack furnaces*, with zig-zag condensers, are employed.

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. 375, which is a glass tube 1·3 m. long and 3 cm. wide. Another good method is to shake with a concentrated solution of potassium permanganate in 6*N* H_2SO_4 containing a little ferric chloride (A. S. Russell) The metal is then distilled in a quartz flask under reduced pressure, a slow stream of air being allowed to bubble through the metal. Other methods are distillation in a good vacuum with a still surface of the mercury (if it bumps, impurities are carried over) or in a current of indifferent gas (Hulett says oxides are carried over if air is used).

FIG. 375.—Purification of mercury.

Mercury is a liquid metal with a silver-white colour. Its density at 0° is 13·5955, and at −185° (solid) 14·383; it boils at 356·9° 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°. 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 nitrate: on adding ammonium citrate it forms a black precipitate, which 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 contain definite compounds, *e g*, $NaHg_2$, KHg_2. Copper, silver, lead, gold, etc, are 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 it used for stopping teeth.

EXPT 1.—Pour a little mercury into a solution of silver nitrate. A tree-like growth of silver amalgam is produced (*arbor dianae*).

Mercury has a very small vapour pressure at room temperature (< 0 0002 mm at 0°; 0·008 mm at 40°, 0·270 mm at 100°), but in laboratory air it becomes covered with an oily film and is practically non-volatile *The vapour is very poisonous*, and the metal should never be heated whilst exposed to the air of the laboratory.

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, but with excess of iodine, red **mercuric iodide**, HgI_2, is formed.

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 corresponds 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 group –Hg–Hg–, in which the metal also has a valency of two, and are therefore analogous to the cuprous compounds, containing –Cu–Cu–. 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: $Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2$. 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 yellow

coating of mercuric oxide, HgO, is formed on it, not black mercurous oxide, Hg_2O

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, and 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, giving the ions $HgCl_3'$ and $HgCl_4''$:

$$2HgCl + HCl \rightleftharpoons HHgCl_3 + Hg\ ;\quad HHgCl_3 + HCl \rightleftharpoons H_2HgCl_4.$$

Mercurous bromide, HgBr, is similar to calomel. The **iodide,** HgI, is formed as a green powder by triturating mercury and iodine. 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 coarse crystalline powder on cooling. It is formed as a white precipitate (solubility 0·6 gm. per litre at 25°) 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. According to Hulett (1904) the pure sulphate is best obtained by electrolysis with a mercury anode in dilute sulphuric acid (1 to 6 by volume). 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 130°, or on exposure to light. $Hg_2CO_3 = HgO + Hg + CO_2$

Mercuric compounds.—The mercuric compounds, HgX_2, are formed by the oxidation of mercurous compounds. Calomel dissolves in *aqua regia*, forming **mercuric chloride**, $HgCl_2$. The mercuric compounds, conversely, may be reduced to mercurous compounds or to metallic mercury. 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 proportion added. $2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$; 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 if a mercury salt is heated with powdered charcoal and sodium carbonate.

Mercuric nitrate 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 quicklime 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: $Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$. 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, $3HgO,SO_3$, sparingly soluble in water and called *turpeth mineral*. This was described by Basil Valentine.

Mercuric oxide.—By adding caustic soda or potash 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, different solubilities (yellow 0·0520 gm., red 0·0515 gm., per litre at 25°), and different dissociation pressures 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 at about 300° in an open flask with a long neck. This form, described by Geber, was called by the alchemists *mercurius praecipitatus per se*, or " red precipitate." It decomposes on heating; if the mercury is kept from condensing an equilibrium is set up: $2HgO \rightleftharpoons 2Hg + O_2$.

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.—Mercury is rapidly attacked even in the cold by dry chlorine, a white crust of mercuric chloride, $HgCl_2$, forming on the metal. The action is more rapid on heating. Mercuric chloride is also called *corrosive sublimate* on account of its very poisonous properties and its volatility (m. pt. 277°; b. pt 302°; 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 in 0·1 per cent. solution for sterilising the hands and instruments in surgery.

The preparation of corrosive sublimate is described by 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 Both corrosive sublimate and calomel were made in China at an early period. Their preparation is described in the *Pen tsao* (1596). Lemery describes the sublimation of mercuric nitrate (obtained by evaporating a solution of mercury in nitric acid) with common salt and calcined green vitriol

The modern process of manufacture was first suggested by Kunckel in 1716. 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 (p. 260), and the solution (in which the salt has the normal mol. wt.) is slightly hydrolysed. 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 ether 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 not acted upon by nitric acid.

The solution of mercuric chloride contains the complex ions $HgCl^{\cdot}$, 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 $Na_2HgCl_4 \rightleftharpoons 2Na^{\cdot} + HgCl_4''$. 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 dissolves in hot solutions of alkali-chlorides forming strongly alkaline liquids $HgCl_2 + 2NaOH \rightleftharpoons HgO + 2NaCl + H_2O$ 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. A mixture of mercuric chloride solution and oxalic acid (in presence of minute traces of iron salts) is reduced 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, $HgCl_2,4HgO$ (black)

Mercuric fluoride, HgF_2, unlike the other halogen compounds, is hydrolysed in the cold nearly completely into HgO and HF, it forms a basic salt, HgF(OH). **Mercuric bromide**, $HgBr_2$, is similar to the chloride.

Mercuric iodide.—This salt, HgI_2, 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 (0·06 gm. per litre at 25°), but more readily in alcohol. It is not decomposed by dilute alkalies.

Mercury periodide, HgI_6, is a brown substance said to be 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, $KHgI_3$ is formed. 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 :

$$HgO + 3KI + H_2O = KHgI_3 + 2KOH$$

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.** With traces of ammonia a brown colour, with larger amounts a brown precipitate of NH_2Hg_2OI, is formed.

Nessler's reagent 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 kept separate, 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 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

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 ammonia and ammonium carbonate 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 $Hg(NO_3)_2$ 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.—The sulphide, HgS, occurs as *cinnabar*, and is the pigment *vermilion*. It is formed by triturating mercury and sulphur with a little caustic potash solution. The black sulphide

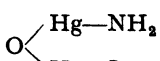
produced slowly becomes red and crystalline. Mercuric sulphide is formed by precipitating a solution of the chloride with hydrogen sulphide: $HgCl_2 + H_2S = HgS + 2HCl$.

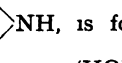
The black precipitate of HgS first formed becomes white if shaken with the excess of mercuric chloride solution, the compound $Hg(HgS)_2Cl_2$ being produced The further action of H_2S changes this into a red and finally a black precipitate (HgS) The black precipitate becomes red on sublimation It is insoluble in boiling hydrochloric or dilute nitric acid, but dissolves in *aqua regia* or in concentrated solutions of potassium or sodium 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: $HgS + Fe = FeS + Hg$.

Mercuric fulminate, $Hg(ONC)_2$ (isomeric with the cyanate) 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 being replaced to some extent by lead azide, $Pb(N_3)_2$

Mercurammine compounds.—The tendency to form complex compounds is very marked in the case of mercury. 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 mercuri-diammonium chloride, $Hg(NH_3Cl)_2$, but is probably an additive compound, $[Hg(NH_3)_2]Cl_2$ 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 **aminomercuric chloride** $NH_2{\cdot}HgCl$, *i e*, mercuric chloride in which one atom of chlorine is replaced by the amino-group NH_2, is formed. This is called *infusible white precipitate*. The brown precipitate obtained by the action of ammonia on Nessler solution is **oxydimercuriammonium iodide**, $(OHg_2)NH_2I$, or NHg_2I,H_2O, or perhaps



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 mercuriammonium salts, $NHg_2{\cdot}OH,2H_2O$. On drying at 125° in ammonia gas, dark-brown explosive $NHg_2{\cdot}OH$, or perhaps  , is formed. Hofmann and Marburg (1899) formulate Millon's base as $(HOHg)_2NH_2{\cdot}OH$, but the formula $HO{\cdot}(Hg_2O){\cdot}NH_2,H_2O$ is now adopted, since it loses H_2O

when dried in ammonia gas and forms $HO{\cdot}Hg_2O{\cdot}NH_2$. Compounds isomeric with the salts of Millon's base were prepared by Franklin (1905) by the action of liquid ammonia on $HgBr_2$ and HgI_2, he regards them as amino-compounds, Hg:N 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 Only mercur*ic* salts form ammines (*i.e.*, addition compounds with ammonia) mercur*ous* compounds are decomposed into mercuric compounds and mercury.

CHAPTER XLIII

VOLTAIC CELLS

Electrical energy.—Electrolysis is accompanied by an absorption of energy. In batteries, chemical reactions occur and chemical energy is transformed into electrical energy: the inverse of electrolysis. H. E. Armstrong supposes that *all* chemical changes are really cases of reversed electrolysis, but the only changes which can furnish electric currents are those involving electrically charged ions, and it is not certain that *all* reactions occur between ions.

In chemical reactions there is usually an evolution of heat, derived from the diminution of chemical energy. 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, but this is not generally the case. The heat evolved in a reaction at constant volume is a measure of the total energy change (p. 345). If the reaction takes place so as to produce an electric current, the energy value of the latter may be less than the diminution of total energy, when the balance is given out as heat; in some cases it may be greater than the change of total energy, when the cell absorbs heat to make up the balance. The energy of the current is 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 (p. 350). Free energy changes refer to some fixed temperature at which the reaction is carried out.

The free energy change is the correct measure of the **affinity** of the reaction. The measurement of free energy changes is most conveniently effected by the electrical method. 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?" The possibility of the measurement of chemical affinity in terms of electromotive force was clearly pointed out by Davy.

Voltage.—Although Faraday's second law shows that the same quantity of electricity, viz., 96,500 coulombs, is required in the decomposition of one gram-equivalent of a compound into its uncharged ions, the amounts of **electrical work** spent in the decomposition of various compounds are very different, corresponding with the different affinities. Electrical energy depends on something besides the

quantity of electricity. The decomposition of a gram-molecule each of hydrochloric acid and hydroidic acid requires electrical energies equivalent to 31·367 k. cal. and 12·361 k. cal. respectively.

Just as the energy of a stream of water is represented by the product of the volume flowing past a given section 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 The electrical pressure is called **electromotive force** or **voltage.** The pressure of water exists whether the stream is flowing or not, and the electric pressure exists between the poles of the battery when the latter is not giving current, it is detected by a sensitive electroscope and 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

Volts × Coulombs = Joules

The work done per second is equal to the quantity of electricity moved per second multiplied by the voltage The quantity of electricity moved per second is the current strength in amperes, 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

Volts × Amperes = Watts

The watt is a small unit, so that in practice the kilowatt, or 1000 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 = volts × amperes × 3·6

The joule is nearly 10^7 ergs, 1 **international joule** = 0·2390 15° g cal., or one 15° g. cal = 4 184 international joules

The minimum voltages required to decompose hydrochloric and hydriodic acids are, on the basis of the numbers given above.

HCl 31,367 × 4·184 − 96,500 = 1·36 volts;
HI 12,361 × 4 184 − 96,500 = 0·54 volt

Voltaic cells.—An arrangement in which the energy of a chemical reaction 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.

Volta's cell consisted 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 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. With the usual convention the direction of the current is from the copper to the zinc outside the cell. Positive electricity passes inside the cell from the

zinc to the copper by transport of positive hydrogen ions moving in this direction. The hydrogen ions deposit on the copper plate, give up their charges to it, and appear as gaseous hydrogen. The discharge is due to removal of free electrons, ϵ, from the copper plate, which neutralise the positive hydrogen ions: $H^{\cdot} + \epsilon = H$

The negative charge taken from the copper is maintained by a current of 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 by the abstraction of electrons from the zinc atoms · $Zn = Zn^{\cdot\cdot} + 2\epsilon$. 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 would have been discharged 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 discharge 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. The two reactions, which when they occur in the same place give out only heat, when they are compelled to take place at two different localities produce a current The reaction in a cell has, therefore, been called "chemical action at a distance"

The voltaic cell does not generate *electricity*. The electrical charges are present in the materials of 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

The Daniell cell.—The Volta cell has the disadvantage that its voltage rapidly decreases when current is taken from it, owing to deposition of hydrogen on the copper, leading to polarisation. In the Daniell cell (1836), the voltage remains practically constant during

action. This cell consists (Fig. 376) 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.

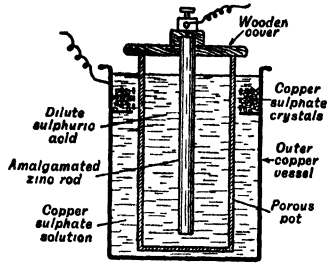


FIG 376 —Daniell cell

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 and 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. $Cu + Zn = Cu + Zn$ Since both ions are bivalent, the reaction involves the transfer of $2 \times 96{,}500$ coulombs, and since the voltage of the cell is 1·1 the free energy of the reaction is $1 \cdot 1 \times 2 \times 96{,}500 = 212{,}300$ joules, which is equivalent to $212{,}300/4{\cdot}184 = 50{,}741$ g 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 g 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, and 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: $Cd + Cu^{\cdot} = Cd^{\cdot\cdot} + Cu$ is different from that in the reaction: $Zn + Cu^{\cdot} = Zn^{\cdot\cdot} + Cu$. 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 a similar reason a change in voltage. *The voltage of a cell depends on the nature of both its electrodes, i.e., of the metals and solutions.*

The voltage also depends on the *concentrations* 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. In a series of Daniell cells composed of Zn in a solution of $ZnSO_4$ containing 1 gm. mol. of $Zn^{\cdot\cdot}$ ions per litre, and other metals in solutions also containing unit concentration of metal ions, different voltages result. In a cell composed of two of these other metals in their solutions, say Cu and Cd, the 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 is 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 owing to its **solution pressure** 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 acquires 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. 377).

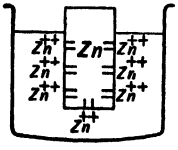


FIG 377.—Diagram illustrating formation of an electrical double layer

The more zinc ions 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.

If a bar of copper is placed in a solution of copper sulphate the copper ions tend, since their osmotic pressure 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 metal surface again puts a stop to this reaction after a certain point

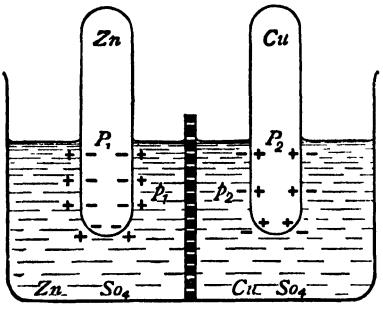


FIG 378 —Theory of the action of a galvanic cell

If the two single electrodes, zinc and copper, are put in communication by a porous partition between the solutions, as in Fig. 378, 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.

The **single potentials** of metals in solutions of their ions containing 1 gm mol per litre are given in the table below The sign attached to the number of volts is that of the charge of the *electrode*. Thus, zinc tends in a molar solution of its ions to throw out still more ions until the metal has a potential *lower* than that of the solution. Copper ions, on the other hand, will tend to deposit from a molar solution, leaving the metal positively charged at a potential above that of the solution. The table is called the **electromotive series** Hydrogen dissolved in platinum or palladium acts like a metal electrode to solutions of acids, containing $H^{\cdot}$ ions Each entry gives the potential difference in volts at 18° between the given electrode and the hydrogen electrode in a solution normal in $H^{\cdot}$ ions The " absolute " potential difference between the hydrogen electrode and a normal solution of $H^{\cdot}$ ions is about 0·274 volt, and the absolute potential of an electrode, referred to

the solution at zero potential, is given by adding 0·274 to the figure in the table.

Electromotive series of the metals.

K	−2 92	Fe(Fe$^{\cdot\cdot}$)	−0 05	As	+0·29
Na	−2 71	Fe(Fe$^{\cdot}$)	−0 44	Cu(Cu$^{\cdot\cdot}$)	+0 345
Ba	−2·84	Cd	−0 40	Bi	+0·2
Sr	−2 74	Tl	−0·34	Sb	+0 1
Ca	−2·5	Co	−0 29	Hg(Hg$_2^{\cdot\cdot}$)	+0·80
Mg	−1 55	Ni	−0·22	Pd	+0·82
Al	−1·24	Pb	−0 12	Ag	+0·80
Mn	−1·04	Sn(Sn$^{\cdot\cdot}$)	−0·14	Au(Au$^{\cdot}$)	+1·5
Zn	−0·76	H	0·00		

The voltage of the Daniell cell with molar solutions is therefore 0·345 − (−0 76) = 1·105, the copper being positive.

Since ionisation takes place by addition of positive charge, one metal will dissolve in a solution of another, displacing the latter, when the electrode potential of the former metal is algebraically smaller.

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 molar solution of zinc ions, is measured by −0 76 volt. Zinc in a solution of cadmium ions will dissolve and cadmium be deposited, since −0·76 − (−0·40) = −0·36; whilst cadmium will deposit copper, since −0·40 − (+0 345) = −0·745 Silver will not deposit copper from a solution of copper ions, since 0 80 − (+0 345) = +0 455 These examples show that the electromotive series is also 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: $Cl_2 \rightleftharpoons 2Cl' + 2\oplus$.

Electromotive series of non-metals.

I	+0·54	Cl	+1·36	SO_4	+1·9
Br	+1·07	OH	+2·20	HSO_4	+2·6
O	+1·60				

Thus, the voltage of the cell: Zn | MZnSO$_4$ | NKBr | Br$_2$, Pt will be −0·76 − (+1·07) = −1·83. The small potential difference between the two solutions is neglected in the above calculations. The potential between solutions containing H$^{\cdot}$ or OH$'$ ions is relatively large.

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 electrolyte, of different concentrations, can form a cell. Cells of this kind are known as

concentration cells. Their voltages do not depend on differences of solution pressures, or affinities, since both electrodes and electrolytes are of the same chemical composition, but on the fact that copper ions, *e.g.*, in a concentrated solution tend to a greater extent to deposit on the copper electrode, on account of the greater osmotic pressure, than copper ions in a dilute solution. The copper plate in the concentrated solution has a greater positive potential than that in the dilute solution, 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.

EXPT. 1.—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. 379. 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.

FIG. 379.—Experiment illustrating the action of a concentration cell.

If electrodes are immersed in solutions which are not of molar 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. mol. per litre, respectively, at 18°, then it can be shown that :

$$P_c = P_o \pm \frac{0{\cdot}058}{n} \log c,$$

where n is the valency of the ion and the correction term has the sign of P_o. Thus, the electrode potential of Zn in a decimolar solution of its ions is $-0{\cdot}76 - 0{\cdot}058/2 = -0{\cdot}789$ volt. It is greater than in molar 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, $K_3Cu(CN)_4$, which ionises as $3K^{\cdot}$ and $Cu(CN)_4'''$, and the direction of the current actually changes sign. On account of the low osmotic pressure of $Cu^{\cdot\cdot}$ ions, copper dissolves with such ease that zinc ions are driven out of solution as metallic zinc.

Colloids.—The particles of colloids are usually electrically charged. The origin of the charge is supposed to be similar to that acquired by metals immersed in liquids, *i e*, ions are attracted from or given off into the solution, and the particles acquire corresponding charges 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 hydrogen sulphide 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 : $Sn'' - 2\epsilon = Sn''''$. 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''' ions touching the plate to Fe'' 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 in 0·2 molar solutions, the sign of the potential is that of the electrode, the normal hydrogen electrode being taken as the standard, as before. The electrodes are platinum plates

Alkaline $SnCl_2$	−0·54	KI	+0·65
Alkaline $NH_2{\cdot}OH$	−0·30	K_3FeCy_6	+0·71
H_2	±0·00	$K_2Cr_2O_7$	+0·82
$NaHSO_3$	+0·42	KNO_2	+0·90
Acid $FeSO_4$	+0·54	$KMnO_4$	+1·52

Decomposition potentials.—Although for the deposition of a gm. equiv. of any ion the same *quantity* of electricity, 96,500 cmb., must pass, the *energy* is different for different ions, and since this is the product of coulombs and volts it follows that the decomposition potentials are different. A Daniell's cell (1·1 volts) will not decompose water, whilst an accumulator (2 volts) will do so.

Since the current through the electrolyte passes only when ions are being deposited, the decomposition voltage is determined by immersing bright platinum electrodes in the solution and applying to them a gradually increasing potential difference by means of a potentiometer circuit. A galvanometer included in the electrolytic circuit shows a sudden large increase in current when decomposition sets in.

When decomposition proceeds reversibly, the decomposition potential is the algebraic difference of the electrode potentials of the two ions, since the electromotive force set up by the products of decomposition, acting as a cell, must be overcome before further deposition can occur.

The voltage theoretically required to decompose molar $ZnBr_2$ solution, for example, is $-0{\cdot}76-1{\cdot}07=-1{\cdot}83$. In practice a larger value is required to deposit an ion than the theoretical electrode potential, especially when a gas such as hydrogen is being liberated: the excess is called the **overvoltage** of the ion. For hydrogen this is very small on platinised platinum, but large on amalgamated lead.

Decomposition voltages in N. solutions.

HNO_3	1·69	NaOH	1·69	$ZnSO_4$	2·35
H_2SO_4	1·67	KOH	1·67	$NaNO_3$	2·15
HCl	1.31	$AgNO_3$	0·70	NaCl	1·98
HBr	0·94	$ZnBr_2$	1·83	$CaCl_2$	1·89
HI	0·52				

The formation of sodium amalgam in the Castner-Kellner alkali cell (p. 204) is possible in spite of the fact that the potential required to deposit sodium is much higher than that normally required to deposit hydrogen. Hydrogen, however, has a large overvoltage on mercury, so that sodium is deposited instead. In order to dissolve the sodium from

the amalgam, with production of caustic soda and hydrogen, the amalgam is brought in contact with metallic iron, on which hydrogen has a smaller overvoltage. Gaseous hydrogen from the water is formed on the iron and the sodium passes into solution as ions, the hydroxide ions of the water also remaining in the solution.

The table shows that in the case of solutions of salts such as NaCl, $NaNO_3$, $CaCl_2$ and alkalies, *when hydrogen and oxygen only are deposited*, the values are practically the same. Le Blanc assumed that in all these cases, although the current is carried through the solution by the ions of the salt, the *ions of water*, $H^{\cdot}$ and OH', being more easily deposited and at a lower voltage than the metal or acid ions, are deposited at the electrodes with formation of hydrogen and oxygen gases. The other ion of water remains in solution at the corresponding electrode, with formation of acid or alkali with the salt anion or cation which has arrived there after carrying the current through the solution to the electrode. The salt ions, being present in much larger amounts than the water ions, transport the current.

In the electrolysis of sodium sulphate we have .

current transport

$$2Na \longleftarrow Na_2 \quad SO_4 \longrightarrow SO_4$$

$$2H_2O \begin{cases} 2OH' \\ 2H^{\cdot} \rightarrow H_2 \end{cases} \qquad \begin{cases} 2H^{\cdot} \\ \tfrac{1}{2}O_2 + H_2O \leftarrow 2OH' \end{cases} 2H_2O$$

electrode deposition

Electrolytic separations.—The electrolytic separation of metals in quantitative analysis depends on the different deposition potentials of the ions. *E.g.*, for copper the *absolute* value is $0{\cdot}274 + 0{\cdot}345 = 0{\cdot}619$ volt, that for zinc is $0{\cdot}274 - 0{\cdot}76 = -0{\cdot}486$ volt. If the potential of the cathode is maintained somewhat below 0·619 volt the copper is first almost completely deposited ; although the decomposition voltage must be increased as the ion concentration is reduced, the change is small and practically all the copper may be removed before any zinc is deposited. The electrode potential is then brought to the value corresponding with zinc deposition, and this metal is deposited on the copper, the latter being first weighed in the platinum dish on which it is deposited, and the zinc is afterwards weighed. If the concentration of copper ions be reduced to a very small value by adding potassium cyanide, which forms complex ions, it is possible to deposit copper and zinc together in the form of brass.

Effect of current density.—The effects produced in electrolysis often depend in a marked degree on the current density at an electrode, this being the current in amperes passing divided by the area of the electrode, usually in square decimetres (1 $dm.^2 = 15{\cdot}5$ $in.^2$) With a small electrode (high current density) the ions near the electrode which are most easily deposited are thrown out of the solution rapidly, and as

diffusion from the rest of the solution to the small volume around the electrode occurs only slowly, other ions with higher deposition voltages may then be thrown out, the deposition voltage of the first ion rising to a high value on account of its very small concentration at the electrode.

It has been found possible, for example, to deposit aluminium and even magnesium along with hydrogen from solutions of their salts by using a high cathodic current density, and when a high anodic current density is used in the electrolysis of sulphuric acid, ozone and persulphuric acid are formed In these cases a much higher electrode potential may be attained than when a low current density is used.

CHAPTER XLIV

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 (a) Sub-group · Metals of the Rare Earths (see p. 888).

The (b) Sub-group : Boron, Aluminium, Gallium, Indium and Thallium

	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Electron configuration	2·3	2 8 3	2 8 18 3	2 8 18·18 3	2·8·18·32 18 3
Density	2 45	2 70	5 9	7 42	11·85
Atomic volume	4·5	10	11 8	15 1	17 2
Melting point	2300°	658 7°	29 75°	155°	303 5°
Boiling point	2550°	1800°	>1600°	>1450°	1650°

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 : $Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$; and $Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$

The metals of the (*b*) 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 : $\overset{I}{M}_2SO_4,\overset{III}{R}_2(SO_4)_3,24H_2O$, which are isomorphous, M being a univalent metal. A true thallic alum has not been prepared.

The element boron, a non-metal, has already been described. The remaining elements, except aluminium, are rare.

ALUMINIUM.

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 Al_2O_3 is found, either anhydrous as *corundum*, or hydrated as *diaspore*, Al_2O_3,H_2O, *hydrargillite* or *gibbsite*, $Al_2O_3,3H_2O$, and *bauxite*, a mixture of diaspore and gibbsite in varying proportions. *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 silicate (clay) pass into the soil :

$$2KAlSi_3O_8 + 3H_2O = Al_3O_3,2SiO_2,2H_2O + 4SiO_2 + 2KOH.$$
$$2KAlSi_3O_8 + 2H_2O + CO_2 = Al_2O_3,2SiO_2,2H_2O + 4SiO_2 + K_2CO_3$$

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

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 known to the Greeks (στυπτηρία) and Romans (*alumen*) ; 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 peculiar 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, who isolated the impure metal, which he called *aluminum*. The pure metal was first isolated by Wöhler in 1827 by the action of potassium on the chloride, $AlCl_3$. Bunsen (1854) prepared aluminium by the electrolysis of the chloride, but the first industrial method of preparation, due

to Deville (1854), depended on the reduction of sodium aluminium chloride by sodium. In 1886 the production 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 $2Al + 3O = Al_2O_3 + 380$ k cal., a large expenditure of energy is required, which can be obtained economically only from cheap water power

Production 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.

In the old process 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, 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 calcined 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 of hydroxide (β-alumina), which is easily washed and on ignition yields pure alumina.

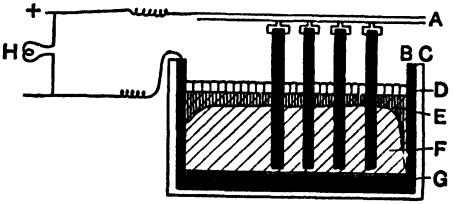


FIG 380.—Electric furnace for aluminium A. carbon anodes, B. carbon lining; C cast-iron vessel, D carbon powder protection; E. crust of solidified electrolyte, F molten electrolyte, G molten metal, H. low voltage charge control lamp

The alumina is then dissolved in fused cryolite and electrolysed between carbon electrodes.

The electric furnace consists of an iron box, 6 ft. by 3 ft. by 3 ft., lined with blocks of carbon, and is made the cathode. The anodes consist of carbon rods set in a row (Fig. 380) 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 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 alumina is electrolysed, the metal (m. pt 659°) forming a pool below the anodes, and the oxygen liberated burning the anodes to CO. Unless a large excess of alumina is present in the bath some cryolite is decomposed and gaseous carbon tetrafluoride, CF_4, is evolved from the carbon anodes. 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. The metal has a purity of 99 per cent. Al, the impurities being chiefly iron and silicon.

Pure aluminium (99 98 per cent.) is made by the **Hoopes' process** A liquid aluminium-copper alloy anode is covered with fused cryolite and barium fluoride, floating on which is a cathode of pure molten aluminium The very pure metal differs in many properties from the 99 per cent. metal

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 parts of motor-cars , it has a high tensile strength. 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 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 is unaltered in dry air, a thin transparent protecting film of oxide being formed. If this film is removed by rubbing the metal with moist 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 a useful reducing agent 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. The *powder* is made by stamping pieces of thin sheet in oil, and really consists of thin flakes.

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 aluminium with evolution of hydrogen. $2Al + 6HCl = 2AlCl_3 + 3H_2$; concentrated sulphuric acid attacks it 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, ship's parts, 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 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 The arrangement is known as an *aluminium rectifier*. It has been replaced by thermionic valves (*i e*, vacuum tubes with electrodes emitting electrons on heating).

Alumina.—Aluminium sesquioxide or alumina, Al_2O_3, the only oxide of aluminium known with certainty, occurs native as *corundum*, which forms rhombohedral crystals nearly as hard as 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 3000°, 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** is produced, soluble in excess of potash or soda, but almost insoluble in dilute 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 (β-alumina) precipitated in Bayer's process has the composition $Al_2O_3,3H_2O$ 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, 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 crystalline rearrangement occurs on heating, and 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 were observed by Berzelius

Bauxite cement (*ciment fondu*) is made by fusing nearly equal weights of bauxite and lime. The clinker is finely ground. This cement, unlike ordinary cement, resists the action of sea-water.

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, lime-water is added to precipitate alumina. Fabrics are 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). 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 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 alumina in acid and alkali, respectively, are mixed, the whole of the alumina may be 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 (blow-pipe 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 : $2Al + 6HCl = 2AlCl_3 + 3H_2$, or by heating the metal or a mixture of alumina and carbon in a current of chlorine :

$$3Cl_2 + Al_2O_3 + 3C = 2AlCl_3 + 3CO.$$

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 Crude aluminium chloride is now largely used in the petroleum industry and is made from bauxite, carbon and chlorine

EXPT. 1.—Heat 10 gm of aluminium turnings in a hard-glass tube connected with a bottle (Fig 381) and pass over the metal a rapid current of chlorine dried by sulphuric acid A sublimate of aluminium chloride is formed

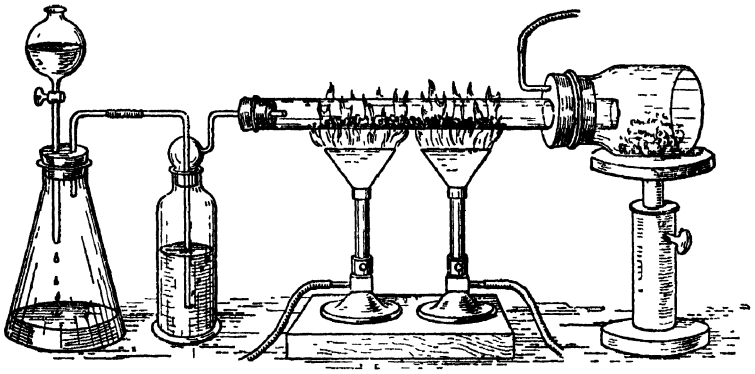


FIG 381.—Preparation of aluminium chloride.

Anhydrous aluminium chloride is a white, crystalline, very hygroscopic substance (usually coloured yellow by ferric chloride as impurity), which fumes in moist air and sublimes at 183° without previous fusion (m. pt. 193° under 2 atm. pressure). The vapour density at 350° corresponds approximately with the formula Al_2Cl_6, but rapidly diminishes with rise of temperature, until at 750° 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 $Al_2Cl_6,C_6H_5NO_2$ in solution in carbon disulphide. On account of its ready volatility and solubility in organic solvents, aluminium chloride in some ways resembles a non-polar compound (*e.g.* PCl_5) rather than a polar salt.

With a little water aluminium chloride forms a crystalline hydrate, $AlCl_3,6H_2O$, more conveniently prepared by dissolving aluminium or soluble 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 $AlCl_3,6NH_3$, and $AlCl_3,SCl_4$;

and double salts, *e.g.*, $NaAlCl_4$, are formed by heating the constituents in a sealed tube.

Aluminium bromide and **iodide** are formed directly from the elements. $AlBr_3$ 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 185°, b pt 350°, vapour density, Al_2I_6, in solution Al_2I_6 Forms a crystalline hydrate, $AlI_3,6H_2O$, and reacts with carbon tetrachloride $4AlI_3 + 3CCl_4 = 4AlCl_3 + 3CI_4$

Aluminium fluoride, AlF_3, formed by dissolving aluminium in excess of hydrofluoric acid, is similar to the chloride but 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 Two forms of the hydrate $2AlF_3,7H_2O$, one soluble, the other insoluble, are described The salt dissolves in hydrofluoric acid, probably forming **hydrofluoaluminic acid**, H_3AlF_6, a salt of which is *cryolite*, Na_3AlF_6

Cryolite, the only commercial source of which is at Ivigtut in South Greenland, is used as a flux in the manufacture of aluminium. It has 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 :

$$2Na_3AlO_3 + 3H_2O + 3CO_2 = 3Na_2CO_3 + 2Al(OH)_3.$$

An artificial cryolite is made by the reaction .

$$2AlF_3 + 6NH_4F + 6NaNO_3 = 2Na_3AlF_6 + 6NH_4NO_3.$$

Aluminium sulphate.—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 hydrates have been described.

Impure aluminium sulphate is made by heating kaolin (clay) with concentrated sulphuric acid, or bauxite with diluted 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. The crude mixture, known as *alumino-ferric*, is used for the

precipitation of colloidal matter from sewage If the ferric is reduced to a ferrous salt, say by hydrogen sulphide, the aluminium sulphate may be crystallised out alone

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 an alkali sulphate, *e g*, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, 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 aluminium sulphate The roasted shale is lixiviated, and after evaporation either ammonium sulphate (originally ammonium carbonate, *i e*, stale urine), or potassium sulphate or chloride, is 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 roasting with fuel, exposing to air, lixiviating and crystallising Alum is also made by adding 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) much more readily than aluminium sulphate. Alum prepared from alunite, called *Roman alum*, although it is pink from the presence of ferric oxide, is quite free from soluble 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 solution is known as neutral alum on heating to 40° it deposits a precipitate of the same composition as natural alunite. 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

$$\overset{I}{M_2}SO_4,\overset{III}{R_2}(SO_4)_3,24H_2O$$

M may be K, NH_4, Na, Rb, Cs, Tl, hydroxylamine, or the radical of an organic quaternary nitrogen base, such as $N(CH_3)_4$. (Li gives no alum.) R may be Al, Fe, Cr, Mn, In, Ga, V, Co, Ti, Mn, Rh, etc.

The radical SeO_4 of selenates may replace SO_4. The alums are not complex compounds, since in solution they give the ions of the component salts. (On pseudo-alums, see p. 953.) 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. The compound $K_2BeF_4.Al_2(SO_4)_3.24H_2O$ is isomorphous with alum.

Aluminium sulphide, Al_2S_3, formed from its elements or by passing sulphur vapour over a heated mixture of alumina and carbon, is *completely* hydrolysed by water: $Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S$, and is not formed by adding ammonium sulphide to a salt of aluminium; in this case aluminium hydroxide is precipitated and hydrogen sulphide is evolved: $Al'' + 3HS' + 3H_2O = Al(OH)_3 + 3H_2S$.

Aluminium nitride.—Aluminium combines directly with nitrogen at 740°, forming the nitride, AlN, in small yellow crystals or as a grey powder. The impure nitride is formed by heating a mixture of bauxite and carbon at 1600° in a current of nitrogen. $Al_2O_3 + 3C + N_2 = 2AlN + 3CO$. 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 was the **Serpek process** for the fixation of atmospheric nitrogen, which is no longer in use.

Aluminium nitrate, $Al(NO_3)_3.9H_2O$, is prepared by mixing solutions of aluminium sulphate and lead nitrate, filtering, and evaporating. Other crystalline hydrates (*e.g.*, with $6H_2O$) 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 solutions.

Ceramics.—The manufacture of *porcelain*, a pure white translucent non-porous ceramic, as hard as steel, appears to have been discovered in China in the seventh or ninth century A.D. It did not reach Europe until 1498. The method of manufacture was discovered in 1709 by Tschirnhaus, or his assistant Böttiger, at Meissen in Saxony, where a factory was started in 1710 although white porcelain was not exhibited until 1713. The French factory at Sèvres was established in 1769. 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 and 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 800°–1000° the mass shrinks, above 1000°, reaction occurs with formation of cristobalite (p. 726) and *mullite*, $3Al_2O_3,2SiO_2$, at 1500° this sinters to a stony mass, which softens at 1650° and at 1740° fuses to a brown or grey viscous liquid

In order to separate from clay the oxide of iron which discolours the product, Schwerin suggested mixing the clay with water and dipping 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 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 ultra-violet 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, 50 parts of kaolin, 30 of felspar and 20 of quartz. It is fired at about 900°, then the glaze is put on and the goods are fired at a bluish-white heat (1300°–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. *English bone china* contains 30–50 per cent. of bone-ash (calcium phosphate).

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.

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 containing 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 30 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, quartz, kaolin and broken porcelain for goods fired at 1400°–1500°; for goods fired at 1300° the proportion of kaolin is reduced and a little calcium carbonate is added In making cheaper earthenware the glaze is put on before firing 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.

The ware may be *painted* either before glazing or some colours are applied on the glaze; the colours are metallic oxides (*e.g.*, cobalt oxide) which form coloured glasses with the glaze or with lead oxide and silica, or borax, applied with the colouring oxide before the glaze is applied

The following table contains one of several classifications 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,
(*e*) *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 are found. In 1826 Guimet obtained artificial *lapis lazuli*, or ultramarine.

A mixture of kaolin, soda-ash or sodium sulphate, sulphur, and resin or wood charcoal is heated to redness in a closed crucible. A **white ultramarine**, with the approximate composition $Na_7Al_3Si_3S_2O_{12}$, is formed in complete absence of air, but usually when air is admitted during heating, a **green ultramarine**, $Na\ Al_3Si_3S_2O_{12}$, 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, 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 and the formulae are rather doubtful

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 hydrogen sulphide 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**, $Ag_6Al_6Si_6O_{30}S_2$, is obtained. Potassium and lithium chlorides give with silver ultramarine the corresponding potassium and lithium ultramarines.

Gallium and Indium.

Gallium and Indium.—The rare element gallium 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 Gallium occurs in traces in bauxite and in commercial aluminium. Middlesborough cast-iron contains 1 part of gallium in 33,000. Gallium fuses at 29·75° and remains supercooled, so that it is often liquid at room temperature Indium 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, $K_2SO_4.R_2(SO_4)_3.24H_2O$.

Thallium.

Thallium.—In 1861 Crookes observed a bright green line in the spectrum of a specimen of flue dust from a vitriol works, which he regarded as due to the presence of a new metal The element was independently discovered, and first isolated in quantity by Lamy in 1862. 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 hydrogen sulphide 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 303·5°; 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 acid 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 and ferric iron, thallous iodide, TlI, resembles lead iodide, PbI_2.

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 830 parts of boiling water (*cf.* PbI_2). **Thallic chloride**, $TlCl_3.4H_2O$, is formed by passing chlorine through thallous chloride suspended in water, and evaporating at 60°.

Thallous hydroxide, $TlOH,H_2O$, is obtained in yellow needles by decomposing a solution of thallous sulphate with baryta-water, filtering, 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 dissolves in concentrated hydrochloric acid and forms $TlCl_3$ (Berry, 1922)

Hydrogen sulphide 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 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.

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, is said to be deposited on the anode in the electrolysis of a solution of Tl_2SO_4 faintly acidified with oxalic acid.

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.

The Rare Earths.

The rare earths.—The substances known as the rare earths are the basic oxides of metals which all 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 mostly in a few special localities. Their compounds are therefore often very expensive and were until the fairly recent discovery of the monazite deposits of India, Brazil and Carolina, in the hands of a small 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.

Crookes, to whom much 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 X-ray spectra of the rare earths have placed their individuality on a 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, into samaria and didymia by Lecoq de Boisbaudran (1879), and the resolution of didymia into

two new earths, neodymia and praseodymia, by Auer von Welsbach in 1885. The " didymium " salts were colourless but in solution exhibited absorption bands in the green and red By repeated crystallisation of the double Na and NH_4 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 nearly 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 often exhibit very beautiful phosphorescent effects on exposure to cathode rays in vacuum tubes, and phosphoresence 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 traces of other earths; gadolinite contains chiefly yttrium, erbium, etc, with only small amounts of cerium and lanthanum.

The rare earths are usually divided into two groups :

I. **Cerite earths** : oxides of cerium, lanthanum, praseodymium, neodymium, illinium, samarium and europium.

II **Gadolinite earths** : oxides of scandium, yttrium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium

The earths called *celtia*, *phillipia*, *mosandria*, *decipia* and *victoria* have proved to be mixtures of the above. Examples of rare earth minerals are *cerite*, $H_2(Ca,Fe)Ce_2Si_2O_{13}$, *orthite*, $AlOHCa_2(Al,Fe,Ce)_2(SiO_4)_3$, *gadolinite*, $(Fe,Be)_2Y_2Si_2O_{10}$, *xenotime*, 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 also Nb, Ta, and Ti; *samarskite*, containing also 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 and are then separated by one or more of the following processes.

(1) Fractional decomposition of the nitrates by heat.
(2) Fractional precipitation with bases
(3) Fractional crystallisation of salts, and double salts with ammonium nitrate, bismuth nitrate, etc.
(4) Fractional precipitation of salts with oxalic acid, succinic acid, sodium stearate, etc.

A separation by fractional crystallisation may be represented diagrammatically by Fig 382, and from this the tedious character of the operation may be inferred A large quantity of solution is allowed to crystallise and six (say) crops of crystals are removed in succession represented by the top row of black dots, leaving a mother-liquor represented by S_1. Each crop is now recrystallised, giving a solid and a mother-liquor represented by dots and circles on the second line

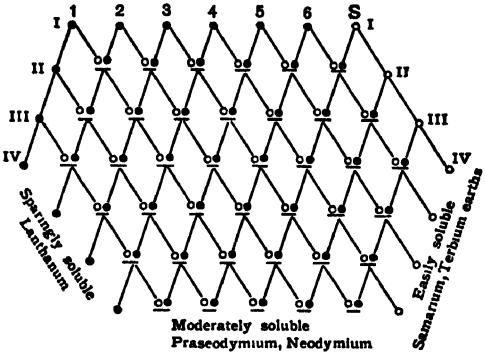


FIG 382.—Diagram illustrating separation of rare earths

The mother-liquor from crop 1 is now combined with the crystals from crop 2, the mother-liquor from crop 2 with the crystals from crop 3, and so on The solutions so formed are again allowed to crystallise and the fractions of the third row are obtained, and so the process goes on

THE RARE EARTH ELEMENTS

	Sc	Y	La	Ce	Pr	Nd	Il	Sm
At no -	21	39	57	58	59	60	61	62
Electron config	2·8 9 2	2·8 18· 9 2	2 8 18· 18 9 2	2·8 18· 19 9 2	2·8·18· 20 9·2	2·8 18 21 9 2	2 8 18· 22 9 2	2·8·18 23 9 2
Density -	—	4·57	6 155	6 78	6 60	7 05	—	7 7
At vol -	—	19 5	22 6	20 7	21 4	20·5	—	19 5
M pt -	—	1475°	810°	630°	940°	840°	—	—
Oxides -	Sc_2O_3	Y_2O_3	La_2O_3	Ce_2O_3 CeO_2	Pr_2O_3 PrO_2 Pr_4O_7, (or Pr_6O_{11})	Nd_2O_3	Il_2O_3	Sm_2O_3
Colour of salts -	colourless	colourless	colourless	CeX_4 orange	green	red violet	—	topaz-yellow

	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
At no -	63	64	65	66	67	68	69	70	71
Electron config	2 8 18· 24 9 2	2 8 18 25 9 2	2 8 18· 26 9 2	2 8 18· 27·9·2	2 8 18· 28 9 2	2·8 18· 29 9·2	2 8 18· 30 9·2	2 8·18 31 9 2	2·8 18· 32·9 2
Oxides -	Eu_2O_3	Gd_2O_3	Tb_2O_3 Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3
Colour of salts -	pale rose	colourless	rose	bright green	rose	deep rose	blue-green	colourless	

The rare earths occupy a place between the strongly basic alkaline earths and weakly basic alumina, the most basic of them being lanthanum oxide. The salts are not usually hydrolysed in solution. Some of the salts and oxides are coloured Traces of a coloured oxide may give an intense colour to a mass of a white oxide in which it exists as impurity 1·5 per cent. of terbium oxide renders gadolinium oxide ochre-brown. The metals are obtained by the electrolysis of the chlorides or fluorides, and are yellowish-white, brilliant and fairly resistant in air. On heating they absorb hydrogen or nitrogen, forming hydrides (*e.g.*, LaH_3) or nitrides (*e g*, LaN). Metallic cerium is obtained in admixture with lanthanum and other rare-earth metals by the electrolysis of the chlorides of the metals in the residues from the extraction of thorium from monazite (p 911). The mixture, called " mixed metal ", is used in alloy with iron in automatic lighters, since when abraded it throws off showers of hot sparks which will ignite coal gas or petrol vapour.

The **hydroxides** are precipitated by alkali and are insoluble in excess (*cf.* aluminium hydroxide) lanthanum hydroxide turns moist red litmus paper blue and absorbs carbon dioxide from the air The **oxides**, generally R_2O_3 (except CeO_2, PrO_2, Pr_4O_7 and Tb_4O_7) are obtained by heating the nitrates, hydroxides or oxalates in air They are mostly amorphous and dissolve in dilute acids even after ignition On the addition of hydrogen peroxide and alkali, **peroxides** are precipitated from solutions of rare-earth salts. The anhydrous **chlorides**, RCl_3, are obtained by igniting the oxides in a stream of chlorine mixed with phosgene or the vapour of sulphur chloride They are soluble in water, alcohol and pyridine. The **sulphides** are hydrolysed by water and can be obtained only by dry methods (*cf.* Al_2S_3).

Cerium compounds are produced in relatively large amounts in the preparation of thorium salts from monazite. Cerium forms two series of compounds, viz , the **cerous salts**, CeX_3, and the **ceric salts**, CeX_4. The cerous salts, in which the element is tervalent, are stable and colourless, usually similar in composition to 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, contains quadrivalent cerium, 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, is a white powder, with a faint yellow tinge if traces of praseodymium salts are present, and 1 per cent. of Pr_2O_3 communicates to ceria a dark brown colour. The commercial oxide is usually yellowish-brown.

The peculiar position of the rare earth elements in the Periodic Table and their chemical properties were explained by Bohr on the assumption that the 4_4 quantum level is empty as far as lanthanum, the electrons going into the higher levels, 5_1, 5_2, 5_3 and 6_1 by preference, since these represent lower energies (Ch XXV). When these levels are occupied the 4_4 level begins to fill up, and as this requires 14 electrons to complete the group of 32 in all the 4-quantum levels, there will be 15 rare earth elements from lanthanum to lutecium, inclusive, each having the same external electron configuration and hence very similar chemical properties, and differing only in the nuclei and the number of electrons in the deep inner levels The following table gives the electronic structures of the atoms, including hafnium, an element in which the 5_3 level now contains 2 electrons which, with the 2 electrons in the 6_1 level, make it quadrivalent, so that it is not a rare earth element, as was at first supposed

	1_1	2_1+2_2	$3_1+3_2+3_3$	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1
La -	2	8	18	2	6	10	0	2	6	1	0	0	2
Ce -	2	8	18	2	6	10	1	2	6	1	0	0	2
Pr -	2	8	18	2	6	10	2	2	6	1	0	0	2
Nd -	2	8	18	2	6	10	3	2	6	1	0	0	2
Il -	2	8	18	2	6	10	4	2	6	1	0	0	2
Sm -	2	8	18	2	6	10	5	2	6	1	0	0	2
Eu -	2	8	18	2	6	10	6	2	6	1	0	0	2
Gd -	2	8	18	2	6	10	7	2	6	1	0	0	2
Tb -	2	8	18	2	6	10	8	2	6	1	0	0	2
Dy -	2	8	18	2	6	10	9	2	6	1	0	0	2
Ho -	2	8	18	2	6	10	10	2	6	1	0	0	2
Er -	2	8	18	2	6	10	11	2	6	1	0	0	2
Tm -	2	8	18	2	6	10	12	2	6	1	0	0	2
Yb -	2	8	18	2	6	10	13	2	6	1	0	0	2
Lu -	2	8	18	2	6	10	14	2	6	1	0	0	2
Hf -	2	8	18	2	6	10	14	2	6	2	0	0	2

Owing to the incomplete inner 4_4 levels from La to Yb, the rare earth compounds are (i) often coloured, (ii) paramagnetic, and are transitional elements in the wider sense The ions Sc^{+++}, Y^{+++}, La^{+++}, Ce^{++++} and Lu^{+++} are, however, not paramagnetic, since they either have no 4_4 electrons at all or else, in the case of Lu^{+++}, have a complete 4_4 group. In the case of Ce^{++++} the single 4_4 electron has functioned as a valency electron and has been removed The ions of the elements from Il to Yb possess 4_4 electrons and are paramagnetic. The "active" electrons, causing colour, present in the 4_4 levels are partly screened by the completed 5_1 and 5_2 levels, and do not, except in the case of cerium, function as valency electrons In the Fe and Cr atoms, however, they are not shielded in this way and can function as valency electrons.

CHAPTER XLV

THE METALS OF THE FOURTH GROUP

The fourth group.—The group contains two non-metals, carbon and silicon, and seven metals. The two sub-groups are

Sub-Group *a* (Even Series)

	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Electron configuration	2·4	2 8 4	2 8 18 4	2 8 18· 18 4	2 8 18 32 18·4
	Diam Graph				
Density	3 52 2 13	2 49	5 366	7 298	11 38
Atomic volume	3 4 5 6	11 4	13 6	16 3	18 2
Melting point	3500°	1420°	958·5°	231 84°	327 4°
Boiling point	4200°	2600°	2700°	2260°	1620°

Sub-Group *b* (Odd Series)

	Ti	Zr	Hf	Th
Atomic number	22	40	72	90
Electron configuration	2·8 10 2 (2 8 8 4)	2 8 18 10·2 (2 8 18 8 4)	2 8 18 32 10 2 (2 8 18·32 8 4)	2 8·18 32 19·9 2 (2 8·18 32·18 8·4)
Density	5 174	6 53	13 07	12·16
Atomic volume	9 3	14 0	13 66	19 2
Melting point	1800°	1700°	1700°	1845°
Boiling point	>3000°	>2900°	3200°	>3000°

The alternative electron configurations in which the different valencies are exhibited are shown in the above table and in later tables of groups of elements.

In Group IV the differences between the odd and even series are ill-defined. The electrochemical characters of the elements are also not very 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. There are several isotopes of tin, with masses from 112 to 124, and of lead.

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, and gaseous hydrides of tin and lead have also been described (Paneth, 1920). All the elements form chlorides, RCl_4, although in the case of lead the stable chloride is $PbCl_2$.

$SiCl_4$, b pt 56·8°, $SiHCl_3$, b pt 31·8°	CCl_4, b pt 76·7°, $CHCl_3$, b pt 61·2°
$GeCl_4$, b pt 86·5°, $GeHCl_3$, b pt 72°	$TiCl_4$, b pt 136·4°
$SnCl_4$, b pt 114·1°	$ZrCl_4$, sublimes
$PbCl_4$, solidifies −15°, decomposes	$HfCl_4$, sublimes
	$ThCl_4$, m pt 820°, sublimes

Carbon, silicon and germanium form the compounds $RHCl_2$, known as chloroforms (ordinary chloroform is $CHCl_3$)

The typical oxides, RO_2, are all known, but many oxides and other compounds besides those corresponding with the type RX_4 are formed. In the cases of C, Si, Ge, Ti, Zr, Th, the stable type is RX_4; 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 complex compounds 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 ores

Tin.

Tin.—It is supposed that some Egyptian hieroglyphics and the word *bedil* in the Old Testament refer to tin, and tin articles as early as the eighteenth Dynasty (*c* 1400 B.C) at least occur in Egypt. The metal is distinctly mentioned by Homer (as κασσίτερος), and Pliny 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 without doubt St. Michael's Mount, Cornwall. The metal was afterwards called *stannum*

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 Cornwall, the islands of Banca and Singkep (Dutch East Indies), the Malay Peninsula and Burma, Nigeria and South Africa, and Bolivia. It occurs either massive or as an alluvial deposit (*stream tin*), and crystallises in tetragonal prisms terminated by pyramids (Fig. 383). 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; it is removed by electro-magnetic separation, or after roasting by heating with soda ash at 600°, when soluble sodium tungstate is formed.

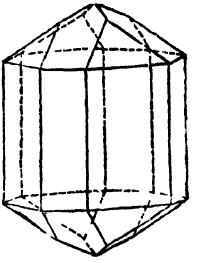


FIG 383.—Crystal of tinstone

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 292). 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 tin as oxide. It is mixed with one-fifth of its weight of ground anthracite and some limestone and sand to form a slag, and is smelted at 1200°–1300° in a reverberatory or a shaft furnace ("Cornish tin-castle") $SnO_2 + 2C = Sn + 2CO$. The slags contain much tin and must be worked up.

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. 787), when the remaining impurities separate as a scum and metal of over 99 per cent. purity is obtained. The scum and dross are worked up by smelting.

Properties.—Metallic tin has a bright white colour, and after fusion a specific gravity of 7·29. When tin is heated to 200° it becomes brittle and can be broken up by a hammer, yielding *grain-tin*. On slowly cooling molten tin, crystals are formed. The metal is not very ductile and too soft to be drawn, but is very malleable and can be rolled into *foil*, when the crystalline structure of the metal is destroyed. A rod of tin emits a peculiar creaking noise when bent, due to the friction of the crystalline particles ("cry of tin": mentioned by Geber). The metal is very fusible but has a high boiling point (2260°). 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. Tin readily alloys with iron and copper. 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 into 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 an open-hearth furnace.

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 being 18° White tin is thus a metastable form under ordinary atmospheric conditions, transformation occurs more easily in contact with a little grey tin. 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

$$\underset{\text{sp gr } 5\ 80}{\text{Grey tin}} \overset{18°}{\rightleftharpoons} \underset{\text{sp gr } 7\ 286}{\text{Tetragonal tin}} \overset{170°}{\rightleftharpoons} \underset{\text{sp. gr } 6\ 56}{\text{Rhombic tin}}$$

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 At a white heat tin burns in air with a white flame.

Tin is only slowly attacked by dilute hydrochloric, sulphuric and nitric 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 **stannic sulphate**, $Sn(SO_4)_2$ (with some basic salt) and sulphur dioxide. Some sulphur also separates, as with zinç.

Concentrated nitric acid when perfectly free from water has no action on tin, but in presence of a trace of water it acts violently, producing red fumes and forming a small quantity of soluble tin salt with an abundant white residue of **metastannic acid**, $H_2Sn_5O_{11}$ (?). Boyle (1675) remarked that "*aqua fortis* eats up more tin than it dissolves." Hot alkalies dissolve tin with evolution of hydrogen, forming stannates. *Aqua regia* readily dissolves it, forming stannic chloride, $SnCl_4$.

Tin forms important alloys, *e g*, *bronze* (p. 789). A mixture of 1 part of lead and 2 parts of tin is ordinary *fine-solder* (*soft-solder* consists of equal parts of tin and lead, cheap solder is 7 lead and 3 tin) *Pewter* contains 4 parts of tin and 1 part of lead, usually with a little antimony. *Britannia metal*, a white metal, consists of tin, antimony and copper. Mirrors are sheets of very clean glass backed by pressing them on a surface of amalgamated tinfoil, although they are now often silvered. Tin forms with copper the definite compounds Cu_3Sn and Cu_4Sn, and with iron $FeSn_2$ *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.

Tin forms two series of compounds the **stannous** SnX_2, and the **stannic** SnX_4, corresponding 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 mixture of solutions 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 $2Fe^{\cdot\cdot\cdot} + Sn = 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}$.

The lower oxide, stannous oxide, SnO, is more basic than the dioxide, SnO_2, but both show feebly *acidic* properties, forming **stannites** and **stannates**, which are largely hydrolysed in solution $Na_2SnO_2 + 2H_2O \rightleftharpoons 2NaOH + H_2SnO_2$ (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 as a transparent glass by passing hydrogen chloride over heated tin. It is soluble in alcohol or ether, melts at 240°, and boils at 603·25°, 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 except in a small amount of water—they dissolve in 0·37 parts at 15°—or unless hydrochloric acid is added: with much water white **stannous oxychloride**, $2Sn(OH)Cl,H_2O$, 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 acid**, $HSnCl_3,3H_2O$ and in solution H_2SnCl_4, are formed. These form stable crystalline salts, *e.g.*, $(NH_4)_2SnCl_4$. Three compounds of $SnCl_2$ with ammonia are known: $SnCl_2,NH_3$; $SnCl_2,2NH_3$ and $3SnCl_2,2NH_3$.

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, m pt 215·5°, similar to the chloride **Stannous iodide**, SnI_2, is a red crystalline substance, m pt 316°, 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 (black when dry) is soluble in hot concentrated hydrochloric acid (arsenic trisulphide is insoluble); 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 $(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + H_2S + SnS_2$

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 1½–2 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 $Sn(NO_3)_2,2OH_2O$.

Caustic soda added to a solution of stannous chloride gives a white precipitate of **hydrated stannous oxide**, $3SnO,2H_2O$ (Bury and Partington, 1922). On heating this loses water and forms **stannous oxide**, an olive-green powder also formed by heating stannous oxalate: $SnC_2O_4 = SnO + CO + CO_2$. It smoulders when heated in air, forming the dioxide, SnO_2. The precipitate is soluble in alkali, forming a solution of a **stannite**, Na_2SnO_2. This solution has strong reducing properties. It is unstable and deposits black SnO on standing. Very

concentrated alkali decomposes hydrated stannous oxide into spongy tin and sodium stannate: $2SnO = Sn + SnO_2$,

Stannic compounds.—When tin is treated with chlorine gas a volatile strongly fuming colourless liquid is produced, **stannic chloride**, $SnCl_4$, discovered by Liebau (Libavius) in 1605, and 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" (most technical names are over a century out of date) or "butter of tin" Stannic chloride is obtained in detinning scrap tinplate (p. 896). 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 at 0°, crystals of **hydrochlorostannic acid**, $H_2SnCl_6,6H_2O$, are formed, melting at 20°. 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 dissolves in water without decomposition. The compounds $SnCl_4,2SCl_4$, $SnCl_4,N_2O_3$, $SnCl_4,2NOCl$, $SnCl_4,PCl_5$, and $SnCl_4$, $POCl_3$ are formed directly.

Stannic bromide, a white fuming crystalline solid, and the **iodide**, red stable octahedral crystals, are formed directly. The **fluoride**, SnF_4, from $SnCl_4$ and anhydrous HF, forms white deliquescent crystals. It forms complex salts, *e g*, K_2SnF_6, analogous to silico-fluorides

	$SnCl_4$	$SnBr_4$	SnI_4	SnF_4
M. pt.	−33°	30°	143·5°	Sublimes
B. pt.	114·1°	201°	340°	705°
Density	2·234(15°)	3·349(35°)	4·696	4·78

Solutions of halogen compounds of quadrivalent tin contain the un-ionised substances and 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, $Sn(OH)_4 \rightarrow Sn(OH)_3 \rightarrow Sn(OH)_2^{\cdot\cdot} \rightarrow Sn(OH)^{\cdot\cdot\cdot} \rightarrow Sn^{\cdot\cdot\cdot\cdot}$. **Stannic phosphate**, $Sn_3(PO_4)_2$, is obtained by adding sodium phosphate to a solution of stannic sulphate containing a little sulphuric acid, as a white amorphous precipitate By dissolving tin in phosphoric acid, crystalline $SnHPO_4$ is obtained. From dilute solutions of

stannic chloride the hydrated dioxide separates as a gelatinous precipitate, especially on boiling $SnCl_4 + 2H_2O \rightleftharpoons SnO_2 + 4HCl$ If the gelatinous form is digested with a solution of potassium sulphate it becomes granular, filters readily, can be washed, and on ignition forms SnO_2

Stannous compounds are oxidised and can be estimated by titration with standard iodine $SnCl_2 + I_2 = SnCl_2I_2$, or ferric chloride $Sn^{\cdot\cdot} + 2Fe^{\cdot\cdot\cdot} = Sn^{\cdot\cdot\cdot\cdot} + 2Fe^{\cdot}$ 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 hydrated stannic oxide 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.*). The only orthostannate known is Ca_2SnO_4.

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 concentrated sulphuric, and does not dissolve in aqueous alkalies It can be brought into solution only by fusion with caustic alkalies or alkali sulphides

If tin is treated with fairly concentrated nitric acid, stannous nitrate, $Sn(NO_3)_2$, appears first to be formed, but is rapidly 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 **meta-stannic acid** It was given 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 They have also been regarded as colloids with particles of different sizes. Cold solutions of alkalies react with β-stannic acid, forming **meta-stannates** (*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 is produced, from which acids throw down α-stannic acid

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 the sol, colloidal β-stannic acid is produced

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 concentrated acid. It is called **β-stannyl chloride**, but may be an adsorption complex or a salt of β-stannic acid, which behaves as a weak base On boiling or adding sulphuric acid β-stannic acid is quickly precipitated The white powder obtained by the action of concentrated nitric acid on tin may be the corresponding nitrate, $Sn_5O_9(NO_3)_2,4H_2O$

If β-stannic acid is heated with water at 100°, it passes into another form called **parastannic 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 ill-defined Metastannic acid adsorbs phosphoric acid almost quantitatively from solutions, and may be used in the separation of this acid in qualitative analysis, although it is not altogether satisfactory

Perstannic acid corresponds with the unknown **peroxide**, SnO_3 By grinding stannic hydroxide with H_2O_2 at 70° and drying the residue, 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.—This compound is formed by precipitating a solution of a stannic salt with H_2S The precipitate is light yellow but becomes black on drying ; it is a mixture of the dioxide and disulphide Crystalline SnS_2, obtained as a residue of golden yellow glistening scales (sp gr 4·425) called *mosaic gold*, by heating a mixture of tin amalgam or filings, sulphur, and salammoniac, as described in a fourteenth-century Naples MS , is insoluble in acids but dissolves in *aqua regia* or alkalies .

$$Sn + 4NH_4Cl = (NH_4)_2SnCl_4 + H_2 + 2NH_3 ;$$
$$2(NH_4)_2SnCl_4 + 2S = SnS_2 + (NH_4)_2SnCl_6 + 2NH_4Cl.$$

Sodium orthothiostannate, $Na_4SnS_4,18H_2O$, is formed by treating sodium stannate solution with sodium sulphide From a solution of it boiled with precipitated SnS_2, the **metathiostannate**, $Na_2SnS_3,8H_2O$, crystallises at room temperature. The metathiostannate is also formed by boiling tin and sulphur with a solution of sodium sulphide.

Tin hydride, SnH_4, is obtained as a gas, mixed with hydrogen by the action of hydrochloric acid on an alloy of tin and magnesium. The pure compound is prepared by electrolysing a solution of tin sulphate containing 0·5 per cent. of dextrin between platinum electrodes, washing the hydrogen (containing 0·01 per cent of SnH_4) with water and alkaline lead acetate solution, drying by passing through tubes cooled at −80° to −100°, and condensing in liquid air, the solid melts at −150° The liquid is then fractionated at low temperatures The gas is stable in a glass vessel for some days at room temperature, but is rapidly decomposed in presence of minute traces of tin and in contact with $CaCl_2$ and P_2O_5. It decomposes rapidly and completely above 150°, does not react with dilute alkali, dilute hydrochloric acid, dilute or concentrated nitric acid, copper sulphate or lead acetate, but is absorbed by concentrated sulphuric acid or concentrated alkali, solid alkali, soda lime and silver nitrate solution (giving a black precipitate containing tin and silver).

LEAD.

Lead.—The metal lead, easily reduced from its ores, was known in ancient Babylonia and Egypt, it occurs in early bronzes, and a small lead statue in the British Museum is attributed to the First Dynasty (3000 B C) Lead is mentioned in Job xix; it was apparently at first confused with tin, but it has a separate name (*μόλιβος*) in Homer and the difference was recognised by Pliny (p. 894). The Greeks obtained lead from the Laurion mines but made little use of it. The Romans obtained lead from Spain, Gaul and Britain, and used it largely for cisterns, water pipes, etc There is a considerable amount of Roman lead at Bath.

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 heavy (sp. gr 7·5), with a bright lustre, and is found in many parts of the United Kingdom, especially in the north ("Crossfell" district), in the north midlands (*e g*, Derbyshire), and south-western counties (Cornwall); it also occurs in Flintshire, and at Leadhills in Scotland The chief sources of lead ores are Broken Hill (New South Wales), Spain, and North America. Galena is generally associated with quartz, calcite, fluorite, and barytes, and usually contains 0·01–0·1 per cent. of silver. The oxides PbO and PbO_2 (*plattnerite*) are rare minerals; and the carbonate, *cerussite* ($PbCO_3$); chlorophosphate, *pyromorphite* ($3Pb_3(PO_4)_2,PbCl_2$); sulphate, *anglesite* ($PbSO_4$); sulphocarbonate, *leadhillite* ($3PbCO_3,PbSO_4$); and basic sulphate, *lanarkite* ($PbO,PbSO_4$), all 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. The process is

carried out largely in reverberatory furnaces (Fig. 357) known as Flintshire furnaces, in use in 1698. The ore is first roasted at a moderate temperature, when a portion of the galena is oxidised to oxide and sulphate:

$$2PbS + 3O_2 = 2PbO + 2SO_2;$$
$$PbS + 2O_2 = PbSO_4$$

The temperature is then raised, a little quicklime is added, and the smelting reaction takes place, the remaining lead sulphide reacting with the two oxidised products:

$$PbS + 2PbO = 3Pb + SO_2,$$
$$PbS + PbSO_4 \rightleftharpoons 2Pb + 2SO_2 \text{ (reversible).}$$

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 Scotch hearth, which has come into use again, viz., 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 formed by reduction of the oxide in the charge $PbS + Fe = FeS + Pb$, the sulphate by the sulphide and carbon, and the silicate by carbon and lime or ferric oxide Lead fume (chiefly PbO) formed during smelting is collected in flues and bag-filters, or by the electrostatic precipitation process

Lead is also extracted by wet processes. The ore is roasted to sulphate, the soluble sulphates of manganese, magnesium, etc, dissolved out, and the lead sulphate dissolved in saturated brine containing chlorine. Sometimes salt is added during roasting, to form $PbCl_2$ The solution is then electrolysed to deposit spongy lead In some cases the raw ore is agitated with hot brine containing hydrochloric acid, the liquid is filtered and the lead chloride deposited is reduced by heating with limestone and coal dust, or by iron.

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) It is then desilverised (p. 800). Lead is refined by electrolysis in a solution of lead silicofluoride, with a little gelatin, when a coherent deposit is formed (Betts' process).

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. 327·4°). The metal boils at 1140° in a nearly perfect vacuum, the vapour is monatomic at 1870°. Lead 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. 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 said to be formed by electrolysis with weak currents. **Colloidal lead** is produced by Bredig's method (arc between two lead poles under water) or by reducing a solution of the chloride with hydrazine in the cold. *Frary metal* for bearings is lead containing 2 per cent. of barium and 1 per cent. of calcium

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. 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, 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 (On the solvent action of water on lead, see p 176)

Lead dissolves readily in dilute nitric acid or in hot concentrated sulphuric acid, forming salts of the bivalent $Pb^{\cdot\cdot}$ ion, 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 liable, is a blue line on the edges of the gums.

Lead suboxide, Pb_2O, is said to be 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 $Pb^{\cdot\cdot} + Pb = 2Pb^{\cdot}$. Pb_2O is formed by reducing PbO with CO at 300° Subhalides, PbCl, PbBr and PbI, are formed by the action of the methyl halides on Pb_2O.

Lead monoxide.—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. Lead monoxide is reduced by carbon monoxide at 100°, by hydrogen at 310° and by carbon at 550°. Litharge obtained in the refining of

silver is largely used in making flint-glass, glazing pottery, preparing lead salts, and 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. Two crystalline forms of PbO exist, a rhombic (yellow) and a tetragonal (red), the first is obtained by heating lead in air, the second by heating the hydroxide or carbonate.

Lead hydroxide, which appears to have the formula $2PbO,H_2O$ or $Pb_2O(OH)_2$, is formed as a white gelatinous precipitate on adding an alkali to a solution of a lead salt. It may be obtained crystalline. It loses water at 145°, forming the monoxide. The hydroxide is slightly soluble in water (as is PbO, which first forms the hydroxide) and the solution turns red litmus blue. It dissolves both in acids and bases, forming lead salts and plumbites, respectively.

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**, *e.g.*, 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 sesquioxide, Pb_2O_3, is 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 or PbO,PbO_2.

Red lead or minium, Pb_3O_4, is formed by roasting white lead or massicot 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 in making flint glass and cements with oil.

Lead dioxide.—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 remains. This oxide is produced when lead compounds are subjected to the action of powerful oxidising agents in presence of alkalies, *e.g.*, 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 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 on the cathode.

The **lead accumulator** consists of two lead gratings, one filled with finely divided lead and the other with lead dioxide, immersed in

dilute sulphuric acid. The following reactions occur during discharge

$$\begin{cases} PbO_2 + 2H^{\cdot} = PbO + H_2O + 2\oplus, \\ PbO + H_2SO_4 = PbSO_4 + H_2O \text{ (anode)}, \\ Pb + SO_4'' = PbSO_4 + 2\ominus \text{ (cathode)} \end{cases}$$

Both plates tend to become converted into lead sulphate, and two molecules of sulphuric acid are withdrawn from the solution in the reactions

The reactions which occur during charging are

$$PbSO_4 + 2\ominus = Pb + SO_4'' \text{ (cathode)},$$

$$\begin{cases} PbSO_4 + SO_4'' + 2\oplus = Pb(SO_4)_2, \\ Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4 \text{ (anode)} \end{cases}$$

The lead sulphate is converted into lead and lead dioxide and two molecules of sulphuric acid are formed in the solution

Lead dioxide is a powerful oxidising agent. A mixture of the dioxide and sulphur ignites on trituration, burning with a brilliant flame and forming lead sulphide. 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 nitric acid and lead dioxide, a pink solution of permanganic acid is formed. This is Crum's test for manganese· $2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$. 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** $4CaO + 2PbO + O_2 = 2Ca_2PbO_4$. This may be obtained in nearly colourless crystals, $Ca_2PbO_4,4H_2O$ 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 The sodium salt is $Na_2PbO_3,3H_2O$ Anhydrous Na_2PbO_3 on heating decomposes into Na_2O and PbO_2, and into Na_2O, PbO and oxygen at 750° The salts are derived from **orthoplumbic acid**, H_4PbO_4, and **metaplumbic acid**, H_2PbO_3 The former is not known in the pure state; the latter is deposited as a black powder on the anode by electrolysing a slightly alkaline solution of sodium lead tartrate.

Minium, or red lead, may be regarded as lead orthoplumbate, $\overset{II}{Pb_2}\overset{IV}{PbO_4}$, lead sesquioxide as lead metaplumbate, $\overset{II}{Pb}\overset{IV}{PbO_3}$—the sesquioxide is in fact formed on precipitating a lead salt with a solution of a plumbate. When calcium plumbate is heated at 250° in dry air, a **perplumbate**, $CaPb_2O_6$, is said to be formed.

Halogen compounds of lead.—Two series of halogen compounds, PbX_2, and PbX_4, the **plumbous** and **plumbic** compounds, respectively (the little known true plumbous compounds correspond with Pb_2O) are known.

Lead dichloride, plumbous chloride, or simply "lead chloride," $PbCl_2$, occurs as the mineral *cotunnite* in volcanic craters. *Mendipite* is $PbCl_2,2PbO$ and *matlockite* is $PbCl_2,PbO$. The chloride 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 $Pb^{\cdot\cdot} + 2Cl' \rightleftharpoons PbCl_2$ (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 (0·91 per cent.) in cold water, more soluble (3·2 per cent) in boiling water; on cooling the hot solution anhydrous needles separate. Lead chloride melts at 498° and boils at 956°, the vapour density at 1070° corresponds with $PbCl_2$. It dissolves in concentrated hydrochloric acid, forming **hydrochloroplumbous acid,** H_2PbCl_4, 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,** $PbCl_2,4PbO$, *Turner's yellow* (1787), used as a pigment, is formed. Lead antimoniate is called *Naples yellow*. *Cassel yellow*, $PbCl_2,7PbO$, 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 (0·06 per cent dissolves at 15°) On boiling, it dissolves (4·34 gm per litre), and on cooling golden-yellow spangles separate It is soluble in a large excess of potassium iodide forming a double salt, $KPbI_3,2H_2O$, decomposed on dilution If starch is added to the solution it becomes blue on exposure to light, indicating decomposition. **Lead chlorate,** $Pb(ClO_3)_2,H_2O$, formed from litharge and chloric acid, 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 addition of ammonium chloride 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, breaks up at once and yellow liquid **lead tetrachloride** or **plumbic chloride,** $PbCl_4$, is deposited (H Friedrich, 1893). 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.

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 $Sn^{\cdot\cdot\cdot}$) to be very

unstable ; the insoluble dioxide is usually formed when the ion might be expected $Pb^{4+} + 3OH^- = PbO_2 + H^+ + H_2O$.

An orange-coloured solution of hydrochloroplumbic acid is formed by the electrolysis of concentrated hydrochloric acid with a lead anode By electrolysis of sulphuric acid, sp gr 1·7–1·8, below 30° with a lead anode in a porous pot, **plumbic sulphate**, $Pb(SO_4)_2$, is formed in yellow crystals decomposed by water $PbSO_4 + SO_4 = Pb(SO_4)_2$, $Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4$ It is probably formed in the lead accumulator **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 $3KF,HF,PbF_4 = 3KF,PbF_4 + HF$, $3KF,PbF_4 = 3KF + PbF_2 + F_2$

Lead sulphide.—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 hydrogen sulphide into a solution of a lead salt. It dissolves in boiling *dilute* nitric acid, with separation of sulphur ; the concentrated acid converts it completely into the insoluble sulphate, $PbSO_4$ PbS dissolves in hot concentrated hydrochloric acid : $PbS + 2HCl = PbCl_2 + H_2S$. The sulphide melts at 1112° 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 859). On diluting a solution of PbS in concentrated hydrochloric acid, $PbS,4PbCl_2$ is precipitated.

Lead pentasulphide, PbS_5, is said to be formed as an unstable purple precipitate on adding a solution of CaS_5 to a solution of a lead salt at 0°.

Lead sulphate.—This salt is formed by adding sulphuric acid or a sulphate 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, since lead acetate is only slightly ionised ($BaSO_4$ is insoluble), or in hot concentrated sulphuric acid ; on cooling the latter solution (6 per cent. $PbSO_4$), crystals of $PbSO_4$ 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 oxidation of the latter. With ammonia, a **basic sulphate**, Pb_2SO_5, or $2PbO,SO_3$, is formed. $PbSO_4,3PbO$ is also known

" Sublimed white lead," a mixture of $75PbSO_4$, 20PbO and 5ZnO, is formed by burning galena containing zinc in an oxidising atmosphere and collecting the fumes.

Lead nitrate.—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 in crystals by boiling a solution of the nitrate with litharge

Lead chromate.—This compound, $PbCrO_4$, 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 and is precipitated in presence of ammonium acetate

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 plumbite 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 analysis 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, $Pb_3(PO_4)_2$ and PbP_2O_7.—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 precipitate of $Pb_3(PO_4)_2$ formed from a lead salt and Na_2HPO_4 is converted on long standing into $PbHPO_4$

Lead borate (77 per cent. PbO), used as a paint drier, is formed as a white precipitate from a lead salt and borax; glassy borates are formed by fusing litharge with B_2O_3. Mixtures of the borates and silicates are present in some 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 poisonous). 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 red lead in hot glacial acetic acid *lead tetra-acetate*, $Pb(C_2H_3O_2)_4$, is formed, and separates in stable white needles. It is decomposed by water, giving PbO_2

Lead carbonate.—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. The **basic carbonate**, $2PbCO_3,Pb(OH)_2$, is prepared as a white pigment called *white lead* (known to Plato as ψιμύθιον).

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 great covering-power If improperly made it is crystalline and has a considerable degree of transparency, its covering power being correspondingly reduced White lead is readily blackened by hydrogen sulphide 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 so-called *Dutch process* (really described by Theophrastos in 300 B.C.) produces the best quality of white lead. Rolls of sheet lead 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 covered and stacked in rows covered with planks and interstratified with horse-dung or spent tan-bark, the fermentation 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) $Pb(CH_3CO_2)_2 + H_2O + CO_2 = PbCO_3 + 2CH_3\cdot CO_2H$.
(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.

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.

Lead hydride, PbH_4(?), is gaseous and is formed in traces when intermittent sparking occurs between a lead-glycerol cement cathode and dilute sulphuric acid, with a potential of 220 volts. It is liquefied by

liquid air; on passing the gas through a heated tube a deposit of lead is formed (Paneth and Norring, 1920).

Germanium.—This 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, m. pt. −165°, b. pt. −126°, is obtained by adding hydrochloric acid to magnesium germanide. Ge_2H_6 and Ge_3H_8 are also formed.

Hafnium.—In 1923 Coster and von Hevesy detected in the X-ray spectra of several minerals lines characteristic of an element of atomic number 72. It is very similar in chemical properties to zirconium, but is more basic: it occurs in appreciable quantities in some zirconium minerals, *e.g.*, in *malacon* and *alvite*. The elements are separated by the fractional crystallisation of the double ammonium fluorides.

Titanium.—This element was discovered by Gregor in 1789 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 procelain, 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.—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 heating the oxide with calcium, or 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 The **tetrachloride**, $ZrCl_4$, is a white solid obtained by passing CCl_4 vapour over ZrO_2 at 800°. The **sulphate**, $Zr(SO_4)_2$, is obtained by dissolving ZrO_2 in concentrated sulphuric acid, evaporating, and heating

Thorium.—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 or artificial silk 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 some kinds of tungsten electric lamp filaments it prevents disintegration of the latter in use The **tetrachloride**, $ThCl_4$, is a white solid obtained by heating ThO_2 to redness in $COCl_2$, or chlorine and S_2Cl_2 vapour The metal is obtained by heating $ThCl_4$ with sodium Thorium is the only element of its subgroup to form a **carbonate**, indicating its more pronounced basic character.

The Gaseous Hydrides.—An examination of the Periodic Table shows that all elements occupying places 1 to 4 before an inert gas (and also boron) can form gaseous hydrides Elements in groups I-IIIa (except boron) give salt-like solid hydrides, such as NaH Beryllium and magnesium resemble zinc in not forming hydrides The volatile hydrides are covalent compounds, whilst the solid hydrides are conducting when fused, the hydrogen behaving as an anion (Li^+H^-) A different group of hydrides comprises the metallic hydrides CuH, Pd_2H and NiH_2. Silver hydride, however, is said to be salt-like and to be produced by the prolonged action of atomic hydrogen on silver foil

I	II	III	IV	V	VI	VII	VIIIa
Li	—	B	C	N	O	F	Ne
Na	—		Si	P	S	Cl	A
K	Ca		Ge	As	Se	Br	Kr
Rb	Sr		Sn	Sb	Te	I	Xe
Cs	Ba	La	Pb	Bi	Po	—	Em
		etc.					

CHAPTER XLVI

THE METALS OF THE FIFTH GROUP

The metals of the fifth 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:

Sub-group *a*, Even Series.		Sub-group *b*; Odd Series (see p 602).	
Vanadium	V	Nitrogen	N
Niobium	Nb	Phosphorus	P
Tantalum	Ta	Arsenic	As
		Antimony	Sb
		Bismuth	Bi

Sub-group *a* (Even Series).

	V	Nb	Ta
Atomic number	23	41	73
Electron configuration	2·8·11·2 (2·8·8·5)	2 8 18·12·1 (2·8 18·8·5)	2·8·18·32·11·2 (2 8·18·32 8·5)
Density	5·8	7·37	16·6
Atomic volume	8·8	12·7	10 9
Melting point	1710°	1950°	2850°
Boiling point	3000°	>3300°	>4100°

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 divison into odd and even series indicated by the periodic classification is not merely arbitrary, is that the members of the even series (V, Nb, Ta) do not form **organo-metallic compounds** with hydrocarbon radicals, whilst the elements of the odd series (P, As, Sb, Bi) 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 the elements form typical **acidic pentoxides**, R_2O_5, the acidic character diminishing with increasing atomic weight. Vanadium, niobium and tantalum combine very readily with oxygen and their compounds are 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 (except antimony and bismuth) are readily

volatilised. In the odd series the gradual transition from typical non-metals to typical metals is very clearly exhibited. Phosphorus is decidedly a non-metal, antimony and bismuth are typical metals, although 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 (except with nitrogen) RX_5 are formed by all elements of this group; some compounds in which the element is bi- and quadri-valent are also known. Thus, vanadium forms a dichloride, VCl_2, and a tetrachloride, VCl_4

ANTIMONY.

Stibnite.—The earliest records mention under various names a substance used as a pigment and for painting the eyebrows. This practice appears to date from prehistoric times; it was used in Egypt at least as early as 3400 B.C. The black pigment came from Arabia, was called *mestem*, *stimmi*, afterwards *stibi*, and, although usually galena, was sometimes native **antimony sulphide**, Sb_2S_3, *stibnite*. In II. Kings ix. 30, the translation of St. Jerome is: "Porro Jezebel introitu ejus audito depinxit oculos suos stibio," but the word *puch* in the Hebrew probably means the red dye *fucus* (φῦκος).

Metallic antimony is found in Queensland. It is very easily reduced from stibnite, and a Chaldean vase of 3000 B C was found by Berthelot to consist of pure metallic antimony. The metal, not specifically referred to by ancient writers, was probably confused with lead Constantinus Africanus (*c* 1050 A D.) 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 Thoelde, see p 27) 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 antimony, stibnite, which occurs in China, France and Italy, is *liquated*, *i.e.*, heated so that the readily fusible sulphide of antimony (m. pt. 548°) flows away from the rock. The sulphide is 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, 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: $Sb_2O_3 + 3C = 2Sb + 3CO$ 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

Pure antimony is prepared by fusing the pentoxide, prepared by the hydrolysis of recrystallised chlorantimonic acid (p. 919), with potassium cyanide

Properties of antimony.—Antimony is a silver-white lustrous metal, sp. gr. 6·67, 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° and boils at 1380°. The vapour densities at 1572° and 1640° correspond with the molecular weights 310 and 284, respectively. These are intermediate between Sb_4 and Sb_2, perhaps $Sb_4 \rightleftharpoons 2Sb_2$; the freezing points of solutions in lead and cadmium correspond with Sb_2 and Sb, respectively.

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** The *pure* metal does not dissolve in concentrated hydrochloric acid in absence of oxygen, but the commercial metal dissolves on heating. It dissolves in hot concentrated sulphuric acid, forming the **sulphate**, $Sb_2(SO_4)_3$. 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, 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 is explosively converted into ordinary antimony with evolution of heat and 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 undergoes change with a hissing noise 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 with lead and tin used for printers' type. The earliest printer, Gutenberg (1436), used metal type, and metal type containing antimony is referred to by Basil Valentine as in common use in 1600. The definite compound, $SbCu_2$, is a beautiful purple alloy.

	Pb	Sb	Sn	Cu	Zn	Bi
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	2·9	—
Pewter - - - -	—	7·1	89·3	1·8	—	1·8
Anti-friction bearing metal - - -	80	8	12	—	—	—

Oxides of antimony.—Antimony forms two series of compounds, SbX_3 and SbX_5 In solution these appear to give the ions $Sb^{\cdot\cdot}$ and $Sb^{\cdot\cdot\cdot}$, although hydrolysis occurs to a large extent Three oxides are known: **trioxide**, Sb_2O_3 (or Sb_4O_6); **tetroxide**, Sb_2O_4 (or SbO_2); **pentoxide**, Sb_2O_5. All the oxides are easily reduced by hydrogen or carbon

Antimony trioxide, Sb_2O_3, occurs native as *senarmonite* in cubic crystals, 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 pale buff on cooling. It fuses at 656°, and volatilises at 1560°, the vapour density corresponding with Sb_4O_6. It dissolves in cold concentrated nitric acid, forming **antimony nitrate**, $Sb(NO_3)_3$, in hot concentrated sulphuric acid, forming **antimony sulphate**, $Sb_2(SO_4)_3$, and readily in dilute hydrochloric acid to form the **trichloride**, $SbCl_3$, or in tartaric acid. 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 boiling 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 said to be 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, the existence of which is not certain, 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 Above 440° it decomposes into Sb_2O_4, and when prepared as described it always contains a little lower oxide.

When antimony is deflagrated in a red hot crucible with potassium nitrate and the residue extracted with warm water, a white powder of **potassium metantimoniate**, $KSbO_3$, remains, which is slowly 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 is precipitated with hot water, or the trichloride or one of the lower oxides treated with nitric acid, the residue after washing and heating at 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 The existence of these acids is doubtful.

The solution of potassium metantimoniate on evaporation deposits crystals up to a certain point, but on further evaporation yields a gummy mass, readily soluble in warm water The solution forms with sodium salts a white amorphous precipitate, possibly $2NaSbO_3, 7H_2O$, 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 one of the least soluble sodium salts, and a solution of potassium metantimoniate (obtained from antimony and nitre as described) may be used as a test for sodium. An **acid potassium antimoniate**, $K_2H_2Sb_2O_7,6H_2O$, or $KH_2SbO_4,2H_2O$, perhaps $KSb(OH)_6$, is obtained by oxidising potassium antimonite with potassium permanganate

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, m pt. 292°
$SbCl_3$, white soft crystals, m. pt. 73·2°, b pt 223·5°.
$SbBr_3$, white deliquescent needles, m pt 93°, b. pt 280°
SbI_3, three forms, two dark-red and a greenish-yellow. M. pt. of stable form 171°.

SbF_5, viscous liquid, b. pt. 155°.
$SbCl_5$, yellow mobile liquid, b pt. 140° with decomposition $SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$

Antimony trichloride—This compound was prepared by Paracelsus by distilling antimony with corrosive sublimate $3HgCl_2 + 2Sb = 2SbCl_3 + 3Hg$ 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 this 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 solution in ether, 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 described :

$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$ (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 or in presence of sodium carbonate, antimony trioxide is formed.

Antimony pentachloride.—This compound is formed by burning antimony in chlorine (H. Rose, 1825), 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. 2·39°). The vapour is slightly dissociated at the boiling point, 140°: $SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$, 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 hot 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 an acid 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 decomposed 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** occurs as the grey mineral *stibnite*, sp. gr. 4·5–4·6. By precipitating a solution of antimony trichloride in hydrochloric acid with hydrogen sulphide, a *red* amorphous precipitate is formed, which if dried at 100° and then heated in carbon dioxide at 200° gives off some free sulphur and forms the greyish-black crystalline modification, sp. gr. 4·652. The red form is used as a pigment (*antimony vermilion*), and in vulcanising rubber, the red varieties of which contain it. It can be obtained by warming a solution of the trichloride with sodium thiosulphate. 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 boiling

concentrated hydrochloric acid; arsenic sulphide is insoluble. 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 hydrogen sulphide 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. 619) 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, $R_4Sb_2S_5$, $RSbS_2$, and $R_2Sb_4S_7$ Precipitated antimony trisulphide is insoluble in ammonium carbonate, whereas arsenic sulphide is soluble (p. 646).

Thioantimoniates.—When antimony trisulphide is boiled with caustic soda and sulphur, the filtered and cooled solution deposits large pale yellow tetrahedral 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: $Sb_2S_3 + 3(NH_4)_2S + 2S = 2(NH_4)_3SbS_4$. 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, or a mixture of **antimony tetrasulphide**, Sb_2S_4, and sulphur, is precipitated:

$$2(NH_4)_3SbS_4 + 6HCl = 6NH_4Cl + Sb_2S_5 + 3H_2S.$$

This forms an orange-red precipitate, mentioned by Basil Valentine and by Glauber (1654) It is prepared by precipitating a solution of Schlippe's salt with sulphuric acid and used, under the name of *golden sulphuret of antimony*, in vulcanising rubber On heating alone or with water or acids, it decomposes into sulphur and the black trisulphide.

Antimony pentasulphide readily dissolves in alkalies, even warm ammonia, and alkali sulphides, forming thioantimoniates:

$$Sb_2S_5 + 3Na_2S = 2Na_3SbS_4;$$
$$4Sb_2S_5 + 24KOH = 5K_3SbS_4 + 3K_3SbO_4 + 12H_2O.$$

It also dissolves in sodium carbonate but not in ammonium carbonate. The pure tetrasulphide is said to be obtained by precipitating zinc thioantimoniate with dilute acid, drying and extracting the free sulphur with carbon disulphide.

Antimony hydride.—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 grey flame, producing fumes of the trioxide. A black stain of antimony is deposited on a cold porcelain dish held in the flame: $2SbH_3 = 2Sb + 3H_2$. This is also formed, on

both sides of the heated spot, on passing the gas through a heated glass tube (arsenic is deposited from arsine 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

A purer gas is obtained by the action of dilute sulphuric acid on an alloy of equal weights of zinc and antimony. Pure stibine is prepared (Stock and Doht, 1901) 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 phosphorus pentoxide, 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 or sometimes spontaneously, as it is strongly endothermic. 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. 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 oxide, 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 dried and heated in a porcelain boat in a stream of carbon dioxide to expel free sulphur. 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:

$$Sb_2O_5 + 4KI + 10HCl = 2SbCl_3 + 4KCl + 2I_2 + 5H_2O.$$

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 **antimonyl** radical, SbO, and is **potassium antimonyl tartrate**, $2K(SbO)C_4H_4O_6,H_2O$. It is also used as a mordant.

Bismuth.

Bismuth.—Metallic bismuth may have been known in antiquity but confused with tin and lead. Agricola (who says it was unknown to the ancients) describes it in his *Bermannus* (1530) under the name of *bisemutum*, in his *de natura fossilium* (1546) he calls it *plumbum cinereum*. Libavius in his *Commentariorum chymicorum*, 1606, mentions it, noting that it was used to soften tin The name is supposed to have been derived from the German *wiesen* (a meadow), given to it by the old miners on account of its reddish 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 diarrhoea and cholera. This substance, known as *pearl white*, was introduced by Lemery as a cosmetic, although it acts injuriously on the skin, as Lemery himself points out. It has now been replaced by zinc oxide or starch.

Bismuth occurs somewhat sparingly, usually in the *native* condition containing arsenic and tellurium, associated with silver and cobalt ores 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 reddish-white metal, sp. gr. 9·80, which readily forms large crystals on cooling the fused metal. These crystals, obtuse rhombohedra resembling cubes, are usually covered with a superficial film of oxide and then exhibit a splendid iridescent play of colours. A trace of tellurium alters its appearance and properties. 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°–65°) 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 1450°, and the vapour density between 1600° and 1700° shows that partial dissociation occurs $Bi_2 \rightleftharpoons 2Bi$. 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). $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$.

Bismuth nitrate.—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.

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 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 hydroxide, $Bi(OH)_3$, is precipitated as a white amorphous powder 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 (greenish-grey when not quite pure) residue of **bismuth trioxide**, Bi_2O_3. This stable oxide of bismuth is obtained by heating bismuth nitrate. It fuses at 820°. The solid formed on cooling to 704° 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.

What was formerly regarded as a black dioxide, Bi_2O_4, is a mixture of Bi_2O_3 with finely divided metallic bismuth. It is thrown down by adding a bismuth salt to a solution of sodium stannite (stannous chloride with excess of caustic soda), often accompanied by a white precipitate of bismuth or stannous hydroxide, and hence the reaction, which is used in the identification of bismuth (or stannous) salts, is called the " magpie test "

Higher oxides of bismuth are precipitated as reddish-brown powders on adding oxidising agents such as potassium ferricyanide or chlorine to alkaline solutions of bismuth trioxide. From a hot solution in dilute alkali, chlorine precipitates a scarlet powder which is principally **bismuth tetroxide**, Bi_2O_4. From the solution in concentrated alkali, chlorine precipitates also some **bismuth pentoxide**, Bi_2O_5. Both these oxides dissolve in nitric acid of sp. gr. 1·2 with evolution of oxygen. By oxidising with ferricyanide or persulphate in concentrated alkali, a small amount of **bismuth peroxide**, Bi_2O_6, insoluble in nitric acid, is formed.

The higher oxides lose oxygen on heating and 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**, perhaps $KBiO_3$, is formed, it 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 sulphate, $Bi_2(SO_4)_3$, is obtained as a white amorphous mass by evaporating the metal with hot concentrated sulphuric acid. It forms a sparingly soluble **basic sulphate**, $Bi_2(OH)_4SO_4$, 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, which 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 quickly decomposes and deposits a black precipitate of bismuth sulphide, Bi_2S_3.

The **basic carbonate**, $2(BiO)_2CO_3,H_2O$, is obtained as a white powder 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 in acid solutions A mixture of Bi_2O_3 and P_2O_5 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 hydrogen sulphide 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.

Thio-salts are produced by dissolving the sulphide in concentrated *potassium* sulphide, or by fusion with sulphides Bi_2S_3 is only sparingly soluble in sodium sulphide The salts $KBiS_2$ and $NaBiS_2$ form fine crystals with a metallic lustre, rapidly oxidised in the air On diluting the solution of the sodium salt, 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. 447°, on passing excess of chlorine over bismuth. Boyle (1663) obtained it by heating bismuth with corrosive sublimate: $2Bi + 3HgCl_2 = 2BiCl_3 + 3Hg$ Its vapour density corresponds with the formula $BiCl_3$. The trichloride is also formed by dissolving bismuth in *aqua regia*, evaporating (when crystals of $BiCl_3,H_2O$ are deposited) and distilling 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, and $BiCl_3,NOCl$ and $2BiCl_3,NO$, are known.

A solution of bismuth chloride when poured into water gives a white precipitate, which can be obtained crystalline, 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.

The black dichloride $BiCl_2$, formed on heating $BiCl_3$ with excess of bismuth, or by heating bismuth with calomel at 250°, is probably a mixture (*cf* Bi_2O_2).

The **tribromide**, $BiBr_3$, m. pt 210°, b. pt 453°, is formed from the elements in golden-yellow crystals, decomposed by water into white BiOBr **Bismuth tri-iodide**, BiI_3, m pt $<439°$, 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.

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 a gaseous bismuth hydride ($?BiH_3$) are formed Thorium C, an isotope of bismuth, when deposited on magnesium also gives a radioactive gaseous hydride on solution in acid

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 meta-vanadate, 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, VO) The metal is obtained by the thermit reaction from V_2O_5, 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 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

CHAPTER XLVII

THE METALS OF THE SULPHUR GROUP

The metals of Group VI.—Group VI of the Periodic System comprises nine elements:

Odd series		Even series	
Oxygen	O	Chromium	Cr
Sulphur	S	Molybdenum	Mo
Selenium	Se	Tungsten	W
Tellurium	Te	Uranium	U
Polonium	Po		

Sub-Group (*b*) (Odd Series).

	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Electron configuration	2·6	2·8·6	2 8·18 6	2·8 18 18·6	2·8·18·32·18·6
Density (solid)	1 4256	2·1	4·8	6·235	—
Atomic volume	11·2	15·3	16 5	20 4	—
Melting point	−218 4°	112 8°	220 2°	452·5°	—
Boiling point	−183°	444·55°	688°	1390°	—

Sub-Group (*a*) (Even Series).

	Cr	Mo	W	U
Atomic number	24	42	74	92
Electron configuration	2·8·13·1 (2·8 8·6)	2·8·18·13·1 (2·8·18·8·6)	2·8 18·32·12 2 (2·8·18·32·8·6)	2 8·18·32·21 9·2 (2·8·18·32·18·8·6)
Density	6·737	9·01	18·72	18 685
Atomic volume	7·7	10·7	9·8	12·8
Melting point	1920°	2620°	3370°	< 1850°
Boiling point	2200°	3700°	5900°	—

At first sight no obvious resemblances exist between the elements of the odd and even series. The former (except Po) are non-metals; the latter are all metals. If we take sulphur as representative of the odd series and chromium 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 formulae:

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,$2CrO_3$)

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 alumimium and iron. The metals chromium and iron are similar, and the oxides Al_2O_3, Cr_2O_3 and Fe_2O_3 are isomorphous These three metals Al, Cr, Fe, 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 bivalent radical UO_2, **uranyl**. Molybdenum and tungsten form a number of complex acids with phosphoric acid, etc.

Chromium.

Chromium.—A red Siberian mineral containing lead was described under the name of *crocoisite* by J. G Lehmann in 1766, 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.

Chromium occurs in small amounts in some iron meteorites. The commonest ore is *chromite*, or *chrome-ironstone*, which is ferrous chromite, $FeCr_2O_4$, or FeO,Cr_2O_3, a spinel (p. 879). 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 mined principally in Greece, 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 Chromite is the source of chromium compounds. If reduced with carbon, lime, and fluorspar in the electric

furnace, *ferrochrome*, iron with 60–70 per cent of chromium, is formed which is used in the manufacture of *chrome-steel* It is not attacked by acids An alloy of chromium, nickel, and iron is used for making armour-plates *Stainless steel* is ordinary steel with 12–14 per cent of chromium and up to 0·7 per cent. of nickel Steels with 17–18 per cent of chromium and 7 per cent or more of nickel are not hardened by quenching and have superior corrosion resistance

Manufacture of chromates.—When finely powdered chromite is strongly heated with an alkali, alkaline carbonate or quicklime, with free exposure to air, the chromium is slowly oxidised to a **chromate**, and the iron to ferric oxide.

$$4FeCr_2O_4 + 8K_2CO_3 + 7O_2 = 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2;$$
$$4FeCr_2O_4 + 8CaO + 7O_2 = 2Fe_2O_3 + 8CaCrO_4.$$

The oxidation occurs more rapidly when the chromite is fused with a mixture of alkaline carbonate and potassium nitrate or chlorate :

$$2FeCr_2O_4 + 4K_2CO_3 + 7KNO_3 = Fe_2O_3 + 4K_2CrO_4 + 7KNO_2 + 4CO_2;$$
$$6FeCr_2O_4 + 12K_2CO_3 + 7KClO_3 = 3Fe_2O_3 + 12K_2CrO_4 + 7KCl + 12CO_2;$$

or with sodium peroxide :

$$2FeCr_2O_4 + 7Na_2O_2 = Fe_2O_3 + 4Na_2CrO_4 + 3Na_2O.$$

The chromate is soluble in water to form a yellow solution.

On the technical scale the fusion with potassium carbonate was formerly used, the yellow solution of potassium chromate being treated with sulphuric acid, when **potassium dichromate**, $K_2Cr_2O_7$, is formed and is readily obtained in bright red crystals :

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O$$

In the modern process, a mixture of 340 lb of finely powdered chromite, 270 lb of sodium carbonate and 360 lb. of quicklime is heated to redness on the hearth of a reverberatory furnace with free exposure to air, when all the carbon dioxide is expelled and sodium chromate produced The function of the quicklime is probably to keep the mass porous and prevent fusion, when the particles of chromite would be coated over and reaction prevented Some chromite generally remains unattacked and a little calcium chromate, which is not readily converted into a soluble chromate, is formed. The sodium chromate is extracted with water, concentrated sulphuric acid is added to the solution, and the sodium sulphate which separates is removed The solution is concentrated to sp gr 1·7 and deliquescent red crystals of sodium dichromate, $Na_2Cr_2O_7,2H_2O$, slowly separate.

The sodium salt is much cheaper and more soluble, but may be converted into potassium dichromate by treatment in solution with potassium chloride. Chromates and dichromates are used as oxidising agents, as mordants in dyeing, and in preparing insoluble pigments.

EXPT 1.—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 the sesquioxide in perfectly dry hydrogen at 1500°, or from chromium sesquioxide with aluminium in the *thermit process*: $Cr_2O_3 + 2Al = Al_2O_3 + 2Cr$. 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 an oxide and aluminium powder in a crucible is ignited by a small cartridge of 15 parts of barium peroxide and 2 parts of magnesium powder placed in a depression in the mixture. This is kindled by a small piece of magnesium ribbon.

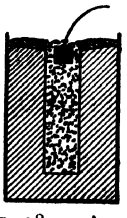


FIG 384.—Arrangement for thermit reaction

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 the dry oxide and aluminium powder is pressed into this, and the (BaO_2 + Mg) igniter placed on the top (Fig 384). 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, and is used in the case of difficultly reducible oxides such as Cr_2O_3.

When chromium oxide is reduced by carbon at very high temperatures, various **carbides**, *e.g.*, 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 hard crystalline but malleable metal, silver-white with a bluish tinge, sp. gr. 6·74, m. pt. 1805°, b. pt. 2200°. It burns brilliantly in the oxy-hydrogen flame, forming the sesquioxide, Cr_2O_3.

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.

Chromium dissolves slowly in dilute sulphuric and hydrochloric acids, especially on heating, forming blue solutions of **chromous salts**:

$Cr + 2HCl = H_2 + CrCl_2$. The blue solutions rapidly absorb oxygen on exposure to air, forming green solutions of **chromic salts**:

$$4CrCl_2 + 4HCl + O_2 = 4CrCl_3 + 2H_2O.$$

Hot concentrated sulphuric acid attacks chromium rapidly; sulphur dioxide being evolved. Dilute nitric acid also dissolves it, 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. The metal is deposited in a thin film by electrolysis from chromic acid solution in *chromium plating*.

Chromous salts.—The chromous salts, CrX_2, contain bivalent chromium and yield the ion Cr''. 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: $Cr''' + H = Cr'' + H'$. This reaction is reversible and chromous salts in acid solution evolve hydrogen, especially in contact with platinum

EXPT 2.—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 385). 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 ($CrCl_2$) The liquid is rapidly transferred through an asbestos filter into a saturated solution of sodium acetate (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 a closed flask.

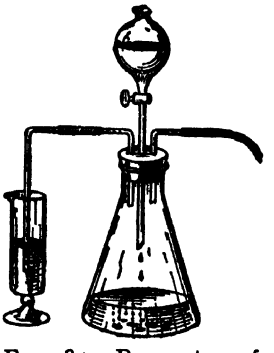


FIG. 385.—Preparation of chromous chloride

The second part of the preparation is more difficult. The air is expelled from the flask by hydrogen, and the solid dissolved in concentrated 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.

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 ($CrCl_2 = 61$, $Cr_2Cl_4 = 122$); 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 or metal in dilute sulphuric acid and cooling the solution. It forms double salts, *e g.*, $K_2SO_4,CrSO_4,6H_2O$. The ammoniacal solution of $CrSO_4$ absorbs acetylene, and the aqueous solution absorbs oxygen and nitric oxide.

Caustic soda added to a solution of a chromous salt in absence of air gives a brownish-yellow precipitate of **chromous hydroxide,** $Cr(OH)_2$, which is readily oxidised in air and in the moist state evolves hydrogen: $2Cr(OH)_2 + 2H_2O = 2Cr(OH)_3 + H_2$. **Chromous oxide,** CrO, cannot therefore be obtained by heating the hydroxide; it is said to be formed as a black powder on exposure of chromium amalgam to air. **Chromous carbonate,** $CrCO_3$, is formed as a grey precipitate when sodium carbonate solution is added to a solution of chromous chloride. With excess of alkali carbonate very stable yellow or red crystalline complex salts are formed, *e.g.*, $K_2Cr(CO_3)_2,1\frac{1}{2}H_2O$ and $Na_2Cr(CO_3)_2,10H_2O$. On boiling with water these are oxidised, with evolution of hydrogen. **Chromous oxalate,** CrC_2O_4,H_2O, is sparingly soluble In the moist state it absorbs only very little oxygen from the air, and when dry it is the most stable chromous salt.

Chromic salts.—The chromic salts are stable compounds containing tervalent chromium, and correspond with the very stable basic **chromium sesquioxide,** or **chromic oxide,** Cr_2O_3. The chromic salts mostly exist in at least two modifications: (i) a *violet* form in hydrated crystals or in solution, the latter containing the chromic ion $Cr^{\cdot\cdot\cdot}$ or probably $[Cr^{\cdot\cdot\cdot}(H_2O)_6]$; and (ii) one or more *green* modifications in which part or all of the chromium is present as a complex ion. With very weak acids, tervalent chromium forms complex salts in which it exists in very stable anions. Another group of complex compounds of tervalent chromium is that of the **ammine** compounds with ammonia, *e g*, $[Cr(NH_3)_6]Cl_3$. In the green solutions there is also, generally, hydrolysis.

Chromic nitrate, $Cr(NO_3)_3$, is stable in the violet form and its solutions only very slowly become green on heating, recovering the violet colour on cooling. The chloride and sulphate, on the other hand, readily form green solutions on heating, and these pass into the violet form only on long standing in the cold. If, however, the acid formed by hydrolysis is nearly neutralised by alkali, and then an acid is added, a violet solution is rapidly formed.

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 sodium dichromate with sulphur in an iron pot and washing out the sodium sulphate from the residue: $Na_2Cr_2O_7 + S = Na_2SO_4 + Cr_2O_3$. 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 ignition of the hydroxide or ammonium dichromate is insoluble in acids but acts as a catalytic agent (*e g*, in the oxidation of ammonia) The crystalline form insoluble in acids may be brought into solution by fusing with potassium hydrogen sulphate or sodium peroxide, or by heating with alkaline permanganate, when a chromate is formed with deposition of manganese dioxide

Chromic oxide is very refractory (m pt. 1990°), but dissolves in fused borax or glass, giving 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 it is a pale greyish-green, flocculent precipitate On standing in contact with a dilute alkali the precipitate slowly " ages " and changes its properties. By precipitating a cold solution of a violet chromic salt with ammonia, a pale blue precipitate which yields $Cr(OH)_3,2H_2O$, or $Cr_2O(OH)_4$, when dried over sulphuric acid, is formed. This hydroxide readily dissolves in caustic soda giving a grass-green solution which may contain a soluble **chromite**, $Na_2Cr_2O_4$. Chromium hydroxide, like aluminium hydroxide, is appreciably soluble in *concentrated* ammonia. Natural chrome-ironstone is ferrous chromite, $FeCr_2O_4$. The green solution may be largely colloidal 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.

According to Siewert (1861) pure chromic hydroxide is precipitated only by ammonia from *boiling* solutions of chromic salts. In cold solutions the precipitate contains an ammonium salt, and if caustic potash or soda is used or if alkali salts are present in the solution, the precipitate contains alkali which cannot be removed by washing. With excess of hot concentrated ammonia, especially in presence of large amounts of ammonium salts, **chromammines**, *e g.*, $[CrCl(NH_3)_4(H_2O)]Cl_2$, are formed and some chromium goes into solution again with a pink coloration.

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 usually

contains boric acid, although a product $Cr_2O_3,2{\cdot}14H_2O$ free from boric acid was obtained by Simon (1929).

Chromic chloride.—Anhydrous chromic chloride is obtained as a sublimate of peach-blossom coloured scaly crystals when chlorine is passed over chromium or a mixture of chromium sesquioxide and carbon heated to redness: $Cr_2O_3 + 3C + 3Cl_2 = 2CrCl_3 + 3CO$. The crystals volatilise at 1065°. They are almost insoluble in cold water and are not attacked by boiling concentrated sulphuric acid, but readily dissolve in water in presence of a trace of chromous chloride (or, less readily, a reducing agent such as $SnCl_2$ or Cu_2Cl_2) giving a green solution.

Three crystalline hydrates, $CrCl_3,6H_2O$, are known, two *green* and one *greyish-blue*. The *first green chloride* is the form most easily prepared; chromic anhydride is boiled with concentrated hydrochloric acid until all the chlorine has been given off $2CrO_3 + 12HCl = 2CrCl_3 + 3Cl_2 + 6H_2O$. The solution is then evaporated until its weight corresponds with less water than $CrCl_3,6H_2O$. It is made up to this weight and cooled The crystals are redissolved in a little water and reprecipitated with ether and hydrogen chloride, when small emerald-green crystals separate.

When the crude salt is dissolved in its own weight of water, boiled half an hour under a reflux, then cooled below 0° and hydrogen chloride in excess is passed into the solution, greyish-blue crystals deposit which dissolve in cold water to a greenish-blue solution. This is the *greyish-blue chloride*.

If ether saturated with hydrogen chloride is added to the filtrate from the greyish-blue chloride preparation, and HCl gas passed through at 10°, the *second green chloride* is precipitated

In solution, the greyish-blue chloride gives three chloride ions, since all the chlorine can be precipitated with silver nitrate. The second green form gives only two chloride ions, and readily loses a molecule of water. The first green form gives only one chloride ion and readily loses two molecules of water. Werner represents the constitution of the three forms as follows:

greyish-blue:	$[Cr(OH_2)_6]Cl_3$;
second green ·	$[Cr(OH_2)_5Cl]Cl_2 + H_2O$.
first 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 the radicals outside are ionisable. 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 hydro-

chloric acid The bromide, $CrBr_3$, and two hydrates, $CrBr_3,6H_2O$, are formed similarly to the chloride. The iodide, $CrI_3,9H_2O$, is unstable

Chromic sulphate.—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 of $Cr_2(SO_4)_3,18H_2O$ are deposited.

By heating potassium dichromate or chrome alum with concentrated sulphuric acid, an olive coloured acid sulphate, $2Cr_2(SO_4)_3,H_2SO_4$, completely insoluble in water and acids, is formed

Chromic sulphate combines with sulphates of the alkali-metals, forming 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 dark 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 3.—Dissolve 20 gm. of potassium dichromate in 150 c c of hot water and after cooling add 4 c.c. of concentrated sulphuric acid Pass sulphur dioxide carefully through the well-cooled solution until the red colour, which at first changes to brown and then to olive-green, has become green-blue

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

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.

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 $Cr_2(SO_4)_3,6H_2O$. The solution is not precipitated either by alkalies or barium chloride and is capable of "masking" the reaction of other sulphate ions. On standing, the solution is transformed slowly into a

violet solution, completely precipitated by barium chloride. Werner represents the forms as follows *violet* $[Cr_2(H_2O)_{12}](SO_4)_3 + 6H_2O$, *green* $[Cr_2(SO_4)_3(H_2O)_6]$ A number of complex chromic-sulphuric acids and other salts are known, some colloidal

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 **Chromicyanides,** *e.g.*, $K_3Cr(CN)_6$ and $Ag_3Cr(CN)_6$, analogous to ferricyanides, and **Chromithiocyanates,** *e.g.*, $K_3Cr(CNS)_6,4H_2O$ (dark red), are stable and crystalline

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 anhydride.—By the action of concentrated sulphuric acid on a solution of a chromate or dichromate, red chromium trioxide, CrO_3, is obtained. This substance is often called "chromic acid," although it is the anhydride of this acid, which 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 colour, 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, although H_2CrO_4 is also no doubt present.

EXPT 4.—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 Buchner funnel containing asbestos with pure nitric acid, and heat to 60°–80° in a current of pure dry air in a tube to remove adhering nitric acid.

A persulphate in *acid* solution converts a chromic salt into chromic acid, and the latter is also formed at a lead dioxide anode in the electrolysis of a chromic salt in presence of fluoride. In *alkaline* solution chromic hydroxide is easily converted into a chromate by many oxidising agents manganese dioxide, lead dioxide, hypochlorite, sodium peroxide and even mercuric oxide $Cr^{+++} + 6OH^- + O = CrO_4^{--} + 3H_2O$ The oxides MnO_2 and PbO_2 are reduced to Mn_2O_3 and PbO

Chromium trioxide forms a deliquescent red woolly mass or red lustrous rhombic prisms, sp gr. 2·7. It melts at 198° to a dark red liquid, solidifying on cooling to a reddish-black mass with a metallic lustre. At 420° 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 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. These may be regarded as chromates in which oxygen of the chromate radical is replaced by CrO_4. $K_2[CrO_3(CrO_4)]$, $K_2[CrO_2(CrO_4)_2]$, etc.

Normal potassium chromate, K_2CrO_4, is obtained in lemon-yellow crystals, m pt. 968·3°, by treating a solution of chromic acid or the dichromate with caustic potash or potassium carbonate, and evaporating. It is isomorphous with potassium sulphate. **Potassium dichromate,** $K_2Cr_2O_7$, 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, m. pt. 396°. The solubilities of the two salts in 100 parts of water are:

	0°	30°	60°	105·6°	104·8°
K_2CrO_4 - -	57·11	65·13	74·60	88·8 (b-pt)	—
$K_2Cr_2O_7$ - -	4·64	18·09	46·10	—	106·2 (b.-pt.)

Both salts are non-deliquescent and 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 and

tends to lose ammonia, forming the dichromate; 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 or carbonates 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, rather difficultly soluble in acids and ammonia.

Barium chromate: $BaCrO_4$; yellow, insoluble in acetic acid, soluble in hydrochloric, nitric and chromic acids.

Zinc chromate (basic). $Zn_2(OH)_2CrO_4,H_2O$, a yellow pigment.

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). $(BiO)_2Cr_2O_7$; orange yellow

Chromic chromate: $Cr_2O_3,CrO_3 = 3CrO_2$ (**chromium dioxide**), and $2Cr_2O_3,CrO_3$—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: $K_2O,2CrO_3 = K_2O + Cr_2O_3 + 3O$.

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 made by dissolving 4·903 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 $N/10$ $K_2Cr_2O_7$) oxidises *two* equivalents of ferrous iron, or 55·8 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.

Chromyl chloride.—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	**tungstenyl chloride,**	WO_2Cl_2
molybdenyl chloride,	MoO_2Cl_2	**uranyl chloride,**	UO_2Cl_2

By the action of concentrated hydrochloric on chromium trioxide in the cold, an oxychloride $CrOCl_3$, possibly containing quinquevalent chromium is said to be formed, double salts of which, *e.g.*, $CrOCl_3$, $3CsCl$, isomorphous with $NbOCl_3,3CsCl$, are known.

When a mixture of sodium chloride and potassium dichromate is distilled in a retort with concentrated (or better, fuming) 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 is also formed by the action of gaseous hydrogen chloride on CrO_3. It boils at 116·7°, and is decomposed violently by water with production of chromic and hydrochloric acids. The vapour density is 5·31 (air = 1), the theoretical density for CrO_2Cl_2 being 5·35. 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 $PbCrO_4$.

Chromyl fluoride, CrO_2F_2, is said to be obtained as a deep red volatile liquid by distilling a chromate with fluorspar and sulphuric acid. It has also been said that the product is CrF_6. No chromyl bromide or iodide is known.

Chlorochromates.—When three parts of powdered potassium dichromate are dissolved in four parts of warm concentrated hydrochloric acid and a little water, 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* (1833); it probably has the constitution $Cl\,CrO_2\,OK$ 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 on heating with evolution of chlorine:

$$4CrO_2(OK)Cl = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_2.$$

Perchromic acid.—If an aqueous solution of chromic acid or of a chromate acidified with sulphuric acid is added to hydrogen peroxide solution, a dark coloured liquid is produced which on agitation with ether gives a deep indigo-blue colour to the latter. This blue ether solution contains a higher oxygen compound of chromium called perchromic acid. On standing over dilute *acid*, the solution in ether slowly loses its colour and the dilute acid becomes green, from formation of a chromic salt On addition of *alkalies*, oxygen is evolved and a chromate is formed.

By the action of organic bases (aniline, pyridine, etc) on the blue ether solution, *deep-blue* salts are formed which are explosive These have been represented as $CrO_4(OR),H_2O_2$, derived from $HCrO_5$, or as acids 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 $(OH)_4Cr(O\,OH)_3$ The red salts may be anhydro-salts of the blue acid

K_3CrO_8 appears to be $\begin{bmatrix} O_2 \text{ v } O_2 \\ Cr \\ O_2 \quad O_2 \end{bmatrix} K_3$

Molybdenum.—The mineral *molybdenite*, found in Queensland, New South Wales and Norway, resembles graphite in appearance but was found by Scheele (1778) to consist of **molybdenum sulphide**, MoS_2 When roasted in air it leaves a residue of **molybdenum trioxide**, MoO_3 (molybdic anhydride), which dissolves in ammonia to form **ammonium molybdate**, $(NH_4)_2MoO_4$ The crystals obtained by evaporation (ordinary "ammonium molybdate") are more complex, $(NH_4)_6Mo_7O_{24},4H_2O$. Molybdenum and tungsten show marked tendencies to form such complex compounds A solution of ammonium molybdate in nitric acid gives with phosphoric acid in the cold a canary-yellow precipitate of $(NH_4)_3PO_4,12MoO_3,2HNO_3,H_2O$, which when heated for some time at 150°–180° leaves ammonium phosphomolybdate, $(NH_4)_3PO_4,12MoO_3$ On gentle ignition a black residue of $P_2O_5,24MoO_3$ is left 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 (2620°) obtained by reducing the trioxide with aluminium Its alloy with iron (ferromolybdenum) is prepared by reducing molybdenite with iron and carbon in the electric furnace; steel containing 2 per cent. or more of molybdenum does not soften on heating and is used for high-speed lathe tools

Tungsten.—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 8). If these minerals are boiled with hydrochloric acid, a yellow powder of **tungsten trioxide**, WO_3 ("tungstic acid") remains If this (or wolfram) is sintered 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 From a solution in the cold, hydrochloric acid precipitates white **α-tungstic acid**, H_2WO_4,H_2O, appreciably soluble in water From hot solutions, yellow insoluble **β-tungstic acid**, H_2WO_4, is thrown down **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 carbon or hydrogen at a red heat ferrotungsten, obtained in the electric furnace, is used for special steels (7–20 per cent. of W, 2–6 per cent of Cr). Tungsten filaments (m pt 3400°) are used in electric lamps. The compounds WF_6 (gas), WCl_6, WCl_5, WCl_4, and WCl_2 are known

Uranium.—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 (40 per cent. of U) are found. All these ores contain traces of radium. 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 this 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_6, 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.

A solution of zinc uranyl acetate is a reagent for sodium (p. 768). A mixture of 100 gm. of uranyl acetate, $UO_2(C_2H_3O_2)_2,2H_2O$ and 60 c.c. of acetic acid is made up to 500 c c. A mixture of 300 gm of zinc acetate, $Zn(C_2H_3O_2)_2,2H_2O$ and 60 c c. of acetic acid is made up to 500 c c. The two solutions are mixed, and the resulting solution after one or two days is filtered

CHAPTER XLVIII

MANGANESE

Manganese.—Sub-group (*a*) of Group VII comprises managanese and two rare elements, masurium and rhenium, sub-group (*b*) contains the halogen elements. The only property in which manganese 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.

GROUP VII.

Sub-group (*a*) even series.	At No.	Electron configuration	Density	At. Vol.	M. Pt.	B. Pt.
Mn - -	25	{2·8·13·2 (2·8·8·7)}	7·39	7·4	1260°	1900°
Ma - -	43	{2·8·18·14·1 (2·8·18·8 7)}				
Re - -	75	{2 8·18·32·13 2 (2·8·18·32·8·7)}				
Sub-group (*b*) odd series:						
F - -	9	2·7	1·14	16·7	−223°	−187°
Cl - -	17	2·8·7	1·66	21·4	−101°	−33·6°
Br - -	35	2·8·18·7	3·187	25 1	−7·3°	58·7°
I - -	53	2 8·18·18·7	4·894	25·9	113·5°	184·35°
—	85	[2 8 18·32·18·7]	—	—	—	—

In its remaining compounds manganese shows close analogies with chromium and iron, the two elements of adjoining groups in the same series. 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, $MnNH_4PO_4$.

Manganese ores.—The most important ore of manganese is the black dioxide, MnO_2, known as *pyrolusite*. This is referred to by Pliny as "magnes," but 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 strongly the oxide with carbon. $MnO_2 + 2C = Mn + 2CO$.

Pyrolusite occurs in many localities such as the Caucasus, Spain, India, and Brazil. It is usually contaminated with ferric oxide and barium, often in the form of *psilomelane*, $(Mn,Ba)O,2MnO_2$, corresponding with Weldon mud, $CaO,2MnO_2$. Pyrolusite always contains less oxygen than corresponds with the formula MnO_2, if used for the manufacture of chlorine by the Weldon process, 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.

Less important manganese minerals are the oxides *braunite*, Mn_2O_3, and *hausmannite*, Mn_3O_4, the hydrated sesquioxide, *manganite*, Mn_2O_3,H_2O; hydrated dioxides, *wad* and *psilomelane*, the carbonate, *dialogite* or *rhodocrosite*, $MnCO_3$, the silicate, *rhodonite*, $MnSiO_3$, and the sulphides *alabandite*, MnS, and *hauerite*, MnS_2. 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. If less than the theoretical amount of carbon is used and the mixture 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 oxide Mn_3O_4 with aluminium in the thermit process (p. 930): $3Mn_3O_4 + 8Al = 9Mn + 4Al_2O_3$. The purest metal is obtained by electrolysis of a concentrated solution of manganous chloride with a mercury cathode, and distilling off the mercury in a vacuum at 250°.

Manganese is a greyish-white, or reddish-white, hard and brittle metal, sp. gr. 7·4, not easily oxidised by air unless it contains carbon. It has a high melting point (1260°), boils at 1900°, and volatilises readily in the electric furnace. 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 **nitrides**, Mn_5N_2 and Mn_3N_2 (also 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* (70–80 per cent of Mn and less than 0·3 per cent. of carbon, for open-hearth steel) and *spiegel* (20–32 per cent of Mn and more than 0·3 per cent of carbon, for Bessemer steel), *manganese steel*, which may contain up to 13 per cent of Mn, is very **hard** and tough It is used for the jaws of rock-crushers and for machinery. *Manganese bronze* is copper alloyed with variable amounts of manganese and zinc. 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 Pure manganese becomes appreciably magnetic only on heating, at room temperature it is paramagnetic

Manganese forms six oxides, the lower oxides being basic and the higher acidic, which give rise to corresponding series of salts

Manganous oxide, $\overset{II}{MnO}$; strongly basic, forming **manganous salts**, $\overset{II}{MnSO_4}$.

Mangano-manganic oxide, Mn_3O_4, or $\overset{II}{MnO},\overset{III}{Mn_2O_3}$, a mixed oxide

Manganic oxide, $\overset{III}{Mn_2O_3}$ feebly basic, forming **manganic salts**, $\overset{III}{Mn_2(SO_4)_3}$.

Manganese dioxide, $\overset{IV}{MnO_2}$, feebly acidic, forming **manganites**, $\overset{IV}{CaMnO_3}$

Manganese trioxide, $\overset{VI}{MnO_3}$, acidic, forming **mangantes**, $\overset{VI}{K_2MnO_4}$

Manganese heptoxide, $\overset{VII}{Mn_2O_7}$; acidic, forming **permanganates**, $\overset{VII}{KMnO_4}$

Manganous chloride.—This salt may be obtained from the residues after the preparation of chlorine from pyrolusite and hydrochloric acid: $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$. 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 as chloride, and the filtered solution on evaporation deposits pink monoclinic crystals of $MnCl_2,4H_2O$, m. pt. 58°: $2FeCl_3 + 3MnCO_3 + 3H_2O = 2Fe(OH)_3 + 3MnCl_2 + 3CO_2$.

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 58·098°, $MnCl_2,2H_2O$ 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. Anhydrous $MnCl_2$ forms a *green* solution in alcohol. It combines with 1, 2 and 6 molecules of NH_3

The **manganous salts**, MnX_2, are derived from bivalent manganese and in solution yield the pale pink cation, $Mn^{··}$. In the solid state they are pink when water of crystallisation is present

Manganous fluoride, MnF_2, is a white powder, hydrolysed in solution, obtained by heating in CO_2 at 300° the white precipitate of $(NH_4)_2MnF_4$ thrown down by a large excess of ammonium fluoride solution from a solution of manganous chloride.

Manganous carbonate.—By adding sodium carbonate to a solution of a manganous salt, a white or pale buff-coloured precipitate of manganous carbonate, $MnCO_3$, is formed, which is sparingly soluble in water containing carbon dioxide to form a bicarbonate, and when moist readily oxidises in air to brown manganic hydroxide, MnO(OH) (*cf* $FeCO_3$). It occurs in the bright red mineral *manganese spar* (*dialogite*) isomorphous with calcite; the mineral *manganocalcite*, $(Mn,Ca,Mg)CO_3$ is isomorphous with aragonite. Manganese carbonate is decomposed by heat.

Manganous oxide.—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, MnO(OH).

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 cc of $N/10$ $I_2 = 0·0008$ gm of O_2

Ammonia precipitates $Mn(OH)_2$ only slowly from a solution containing ammonium chloride. Probably the reaction is similar to that with magnesium salts (p. 839), but the solution rapidly deposits MnO(OH) 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.—This compound, MnS, occurs as the mineral *alabandite*. It is formed as a grey mass by heating the carbonate with sulphur, or the oxide, carbonate or sulphate in hydrogen sulphide;

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. 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.

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 sulphate.—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° (when the solubility is a maximum), $MnSO_4,H_2O$ 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, $(NH_4)_2SO_4$, $FeSO_4,6H_2O$, and the pseudo-alum, $MnSO_4,Al_2(SO_4)_3, 24H_2O$, occurring as the mineral *apjohnite*.

Manganous ammonium phosphate.—This compound, $MnNH_4PO_4$, H_2O, is formed as a reddish-white glittering crystalline precipitate by the addition of ammonium chloride, ammonia, and sodium phosphate to a solution of 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 100°–120°, and at higher temperatures gives MnO.

Manganese borate, of variable composition, is formed as an almost white powder by precipitating manganous sulphate with borax and drying at 100°. 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.—Manganic oxide, Mn_2O_3, occurs in the mineral *braunite*; the **hydroxide**, occurring in the partly dehydrated form as *manganite*, MnO(OH), water 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*, $Cs_2SO_4,Mn_2(SO_4)_3,24H_2O$.

Manganic phosphate, $MnPO_4,H_2O$, 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 complex salts of these two higher chlorides are known, *e g*, K_2MnCl_5 and K_2MnCl_6, the latter being obtained by the action of very concentrated hydrochloric acid on potassium permanganate.

If manganese dioxide is suspended in carbon tetrachloride and dry hydrogen chloride passed through, a solid containing $MnCl_3$ is formed. If the solid is washed with dry ether, a violet solution of manganese trichloride is obtained The residue was formerly considered to contain the tetrachloride, soluble in absolute alcohol to a red solution, but this could not be confirmed.

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 trifluoride, MnF_3, is obtained as a trihydrate by dissolving the sesquioxide in hydrofluoric acid, and the tetrafluoride is known in the form of complex salts, *e g.*, K_2MnF_6.

Mangano-manganic oxide.—The oxide Mn_3O_4, 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: $3MnO + O = Mn_3O_4$; $3MnO_2 = Mn_3O_4 + O_2$. At lower temperatures Mn_2O_3 is formed. 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 Boiling nitric acid decomposes it according to the equation $Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O$, so that it also behaves as $2MnO,MnO_2$.

Manganese dioxide.—This oxide occurs native as *pyrolusite*. It is prepared in the pure state by heating 600 gm of manganous nitrate until red fumes appear, decanting the clear liquid from the residue of lower oxides, and heating it for forty or 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 $CaO,2MnO_2$, and perhaps $MnO,MnO_2(Mn_2O_3)$ A colloidal solution of MnO_2 is obtained by the action of ammonia on boiling permanganate solution.

The commercial dioxide, used as an oxidising agent, 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 rapidly heated with concentrated hydrochloric acid in a small flask, and the chlorine evolved passed into a solution of potassium iodide contained in two U-tubes 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, or by oxidising $MnSO_4$ in warm sulphuric acid by the calculated amount of permanganate and concentrating. The solution in sulphuric acid decomposes at 80°, giving $Mn_2(SO_4)_3$. It is an oxidising agent.

Besides its use in decolorising glass, manganese dioxide is applied (mixed with ferric oxide), as a dark brown glaze to pottery, and as a depolariser in the **Leclanché cell.** This consists of a rod of zinc immersed in a concentrated solution of ammonium chloride, in which is also placed a porous pot containing a carbon rod surrounded by a granular mixture of crushed pyrolusite and carbon. In a second form, the pyrolusite is formed into blocks, one of which is placed on each side of a carbon plate, being held in position by rubber bands. In the dry cell

the ammonium chloride solution is gelatinised by adding glue, the 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 chloride: $Zn + 2NH_4Cl = ZnCl_2 + 2NH_3 + H_2$ 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 :

$$MnO_2 \text{ (solid)} + Aq \rightleftharpoons Mn(OH)_4 \text{ (dissd)} \rightleftharpoons Mn^{\cdots\cdot} + 4OH'$$
$$Mn^{\cdots\cdot} + H + OH' \rightleftharpoons Mn^{\cdots} + H_2O$$
$$Mn^{\cdots} + 3OH' \rightleftharpoons Mn(OH)_3 \text{ (dissd)} \rightleftharpoons Mn(OH)_3 \text{ (ppd.)}.$$

The compound $ZnCl_2,2NH_3$ slowly separates in crystals on the zinc rod. The cell rapidly polarises, but recovers fairly quickly on standing. It is used when weak currents or intermittent currents of short duration are required

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 $Na_2SO_4,10H_2O$ 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 a 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. $3K_2MnO_4 + 2H_2O + 4CO_2 = 2KMnO_4 + MnO_2 + 4KHCO_3$

Potassium permanganate may be obtained from the manganate by passing chlorine through the solution. $2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$

If a *pure* alkali is added to the purple solution of permanganate no reaction occurs, but as commercial alkali usually 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, this reaction occurs spontaneously and oxygen gas is evolved.

The formation of manganates and permanganates by the above reactions was discovered by Glauber in 1659, on account of the colour changes which it undergoes the manganate was called *mineral chameleon*

by Scheele The salts were investigated by Forchhammer in 1820 and by Mitscherlich in 1832, who showed that the green and purple salts were derived from **manganic acid**, H_3MnO_4, and **permanganic acid**, $HMnO_4$, and that the salts are isomorphous with sulphates and perchlorates, respectively.

EXPT. 1.—A powdered mixture of 50 gm. of caustic potash and 25 gm. of potassium chlorate is fused on one iron sand-bath covered with a second one. To the fused mass 50 gm. of finely powdered pyrolusite are added gradually, stirring with an iron rod. The heating is continued until the mass stiffens. It is cooled and extracted with 1 litre of water. The liquid is boiled and carbon dioxide passed in until a drop of the liquid placed on filter paper gives a purple colour (no green). The liquid is allowed to settle, filtered through asbestos, evaporated to 300 c.c. and filtered hot through asbestos. On cooling potassium permanganate crystallises. A further crop is obtained by evaporating the mother-liquor to 100 c.c.

Permanganic acid.—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 or nitrate with sodium bismuthate or 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, very unstable violet crystals of which are formed by evaporation in a vacuum. The acid is a powerful oxidising agent; it is unstable and the solution decomposes with evolution of oxygen and deposition of manganese dioxide: $4HMnO_4 = 4MnO_2 + 2H_2O + 3O_2$. When the solution is shaken with hydrogen or carbon monoxide the gas is absorbed and oxygen evolved.

Manganese heptoxide or permanganic anhydride.—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, and should never be prepared in quantity. When treated with ice-cold water, dark brown drops of manganese heptoxide, Mn_2O_7, the anhydride of permanganic acid, separate:

$$2KMnO_4 + 2H_2SO_4 = (MnO_3)_2SO_4 + K_2SO_4 + 2H_2O.$$
$$(MnO_3)_2SO_4 + H_2O = Mn_2O_7 + H_2SO_4.$$

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. With water it forms a violet solution of

$HMnO_4$, but some decomposition occurs. 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 (Dumas, 1827). 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 chlorine and manganese dioxide. The corresponding **fluoride**, MnO_3F, was prepared by Wohler (1827)

The oxide MnO_3 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 by the action of the water produced by the interaction of H_2SO_4 and Na_2CO_3 (Lankshear, 1912).

Potassium permanganate.—This important salt, made as previously described, forms deep purple-red brilliant rhombic prisms, which 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 it is quite 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: $2K_2MnO_4 = 2K_2MnO_3$ (manganite) $+ O_2$

Potassium permanganate is also made from the manganate by the electrolytic oxidation of the solution between iron or nickel electrodes separated by a diaphragm: $2K_2MnO_4 + H_2O + O = 2KMnO_4 + 2KOH$. 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, but the yield is small.

Calcium permanganate, $Ca(MnO_4)_2$, is obtained by the addition of lime to a solution of permanganic acid obtained by electrolytic oxidation It is a deep violet hygroscopic powder, readily soluble in water. It loses oxygen more readily than the potassium salt. **Sodium permanganate** crystallises only with difficulty · a solution is used as a disinfectant. A solution of permanganate is sold as *Condy's Fluid*.

Potassium permanganate 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* the permanganate is first reduced to green manganate. The solution then deposits brown managanese dioxide and becomes colourless:

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + O;$$
$$2K_2MnO_4 + 2H_2O = 2MnO_2 + 4KOH + 2O.$$

Hence two molecules of permanganate in alkaline solution give *three* atoms of available oxygen when reduced to manganese dioxide.

$$2KMnO_4 = K_2O,Mn_2O_7 = K_2O + 2MnO_2 + 3O.$$

Alkaline permanganate oxidises iodides to iodates:

$$2KMnO_4 + H_2O + KI = 2MnO_2 + 2KOH + KIO_3$$

A manganous salt is oxidised in *neutral* solution in presence of zinc sulphate and zinc oxide to manganese dioxide (which forms $ZnO,2MnO_2$):

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

(2) In *acid solutions* permanganate is reduced to a manganous salt and *five* atoms of oxygen become available from two molecules of permanganate

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O;$$
$$\text{or } 2KMnO_4 = K_2O,Mn_2O_7 = K_2O + 2MnO + 5O.$$

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.

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

Hydrogen sulphide reacts with *neutral* 1 per cent permanganate

$$10KMnO_4 + 22H_2S = 3K_2SO_4 + 10MnS + 2K_2S_2O_3 + 22H_2O + 5S.$$

At the beginning of the reaction some dithionate is formed.

The reaction with hydrogen peroxide has been described (p. 132). The reactions are accelerated by the presence of manganous salts, which act catalytically

EXPT 2.—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 8 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 $5O$; ∴ a normal solution will contain $\frac{2KMnO_4}{5 \times 2}$ gm., and a

decinormal solution $\frac{2KMnO_4}{5 \times 2 \times 10} = 3\ 161$ gm per litre The solution may be standardised by oxalic acid. In the oxidation of ferrous salts, 2FeO require O to form Fe_2O_3, or 55·8 gm of iron require 8 gm of oxygen; hence 1 c c. of $N/10$ $KMnO_4 = 0\ 00558$ gm. of Fe.

In presence of free hydrochloric acid, chlorine may be evolved

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

This may be prevented in titrations by adding a few grams of manganous sulphate and titrating in the cold. The manganous salt greatly increases the velocity of the primary reaction (*e g.*, oxidation of ferrous salt), but not that of the oxidation of hydrochloric acid.

Manganese alums.—Tervalent manganese is capable of replacing aluminium in alums, which are formed from manganic sulphate, $Mn_2(SO_4)_3$, and sulphates of alkali-metals. The potassium alum, $K_2SO_4,Mn_2(SO_4)_3,24H_2O$, forms violet octahedral crystals, but it is (like the corresponding ammonium alum) hydrolysed by water with precipitation of hydrated manganic oxide and is difficult to obtain in the pure state. The rubidium and caesium alums, especially the latter, $Cs_2SO_4,Mn_2(SO_4)_3,24H_2O$, are more stable and crystallise well. All these alums are isomorphous with common alum.

Manganous sulphate, $MnSO_4$, cannot form true alums, but it combines with aluminium sulphate to form what is sometimes called a **pseudo-alum**, in which bivalent Mn replaces the univalent element of the true alums, viz. $MnSO_4,Al_2(SO_4)_3,24H_2O$. Similar compounds (which are not isomorphous with true alums) are formed with ferrous, copper, zinc and magnesium sulphates, *e g.* $ZnSO_4,Al_2(SO_4)_3,24H_2O$.

A list of elements forming alums was given on p 882. The stabilities of the different alums vary with the nature of the elements, generally increasing with the atomic weight of the univalent metal (Cs > Rb > K > Na), and decreasing with increase of atomic weight of the tervalent element. Titanium forms alums only with rubidium and calsium sulphates, and the existence of a true indium alum has been questioned.

Cyanogen compounds.—Potassium cyanide gives with solutions of manganous salts a yellowish-grey precipitate, sometimes said to be **manganous cyanide**, $Mn(CN)_2$, and sometimes $KCN,Mn(CN)_2$ 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 and the corresponding salts are isomorphous.

Masurium and rhenium.—These two higher members of the manganese group (Noddack, Tacke and Berg, 1925) occur in minerals of elements of groups on each side, viz., in *columbite*, a mineral containing

tantalum, and in platinum ores, but only in very small quantities. They were first identified by the X-ray spectra, but rhenium and its salts were later isolated and examined. The chemistry of rhenium has been investigated by Noddack, and by Briscoe and Robinson and collaborators Rhenium forms three **oxides** ReO_4, Re_2O_7 and ReO_2 The tetroxide is white, melts at 26°-30°, and is stable in air up to 150°, when it loses oxygen and leaves Re_2O_7. Rhenium heptoxide is yellow, melts at about 150°, and appears to boil at about 450°. The dioxide, ReO_2, is black and differs from the higher oxides in being non-volatile. Rhenium forms two **sulphides**, Re_2S_7 and ReS_2, both black, the disulphide being useful for the quantitative estimation of rhenium.

The metal, which resembles tungsten or osmium powder and is stable in air, is obtained quite easily by heating the oxide or sulphide in hydrogen. It has a high melting point (over 3000°) and specific gravity (21·2). The atomic weight is 186·31.

The **tetrachloride**, $ReCl_4$, is obtained from the metal and chlorine as a black crystalline substance, volatile on heating in chlorine. It is hydrolysed by water and, like osmium tetrachloride, yields **rhenichlorides** of the type M_2ReCl_6, the potassium salt in particular being well characterised.

The higher oxides dissolve in water to give a solution of **per-rhenic acid**, $HReO_4$, which yields the best characterised compounds of the element, the **per-rhenates**. The per-rhenate ion is colourless, and the potassium salt, which may be melted without decomposition, is much less soluble than the sodium salt (compare the permanganates).

Electronic structures of manganese compounds.—The electron configuration of the manganese atom is

2/2·2 4/2·2 4·5/2 total 25

the third quantum group containing 13 electrons The loss of the two 4-quantum electrons gives the Mn^{++} ion. The other ions of different valency, including the ions of oxy-acids (manganite, manganate and permanganate ions) are formed by drawing upon the 3-quantum electrons as valency electrons

Mn^{++}	2/2 2·4/2·2·4·5/	total 23	valency 2
Mn^{+++}	2/2·2·4/2 2·4·4/	,, 22	,, 3
MnO_4^{----}	2/2·2 4/2 2·4·3/4 (4)	,, 29	,, 4
MnO_4^{--}	2/2 2·4/2 2 4·1/6 (2)	,, 27	,, 6
MnO_4^{-}	2/2·2·4/2·2·4/7 (1)	,, 26	,, 7

The numbers in brackets ( ) denote the electrons gained from hydrogen or metal atoms, which become cations. Some of the oxygens are attached by semipolar double bonds (p. 352), 2 in MnO_4'' and 3 in MnO_4'.

CHAPTER XLIX

IRON

The transitional elements.—The eighth group of the Periodic System comprises those elements which were called by Mendeléeff the *transitional elements.*

Elements of Group VIII.

	At No	Electron configuration	Density	At Vol	M Pt	B Pt
Iron	26	2·8·14·2 (2·8·13·3)	7·85	7·1	1533°	3000°
Cobalt	27	2·8·15 2 (2·8·14·3)	8 718	6 8	1480°	2900°
Nickel	28	2·8 16 2	8 9	6 6	1452°	2900°
Ruthenium	44	2 8 18 15 1 (2 8·18 8·8)	12·26	8 3	2450°	2700°
Rhodium	45	2 8 18 16·1 (2 8·18·14·3)	12·1	8·5	1970°	2500°
Palladium	46	2·8·18 18·0 (2·8·18·16·2)	11 9	9·0	1557°	2200°
Osmium	76	2·8 18·32 15·1 (2 8 18 32·8 8)	22·48	8·5	2500°	5300°
Iridium	77	2·8·18·32·16 1 (2·8 18·32·14 3)	22·42	8 6	2450°	4800°
Platinum	78	2·8·18·32 18·0 (2·8·18 32 14·4)	22·5	8 7	1755°	4300°

The atomic weights of the members of each of the three groups differ little from one another, a behaviour similar to that shown by the rare earth elements (p. 413).

The physical and chemical properties of the elements are also closely related; the platinum metals are very similar and are difficult to separate, as are also cobalt and nickel. The elements in the vertical columns (p. 411) 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 should be, according to the position in the Periodic System, RO_4, but this is confined to ruthenium and osmium. All the elements form lower basic oxides

The elements iron, cobalt and nickel are magnetic metals with high melting points, oxidise in the air at a red heat, and decompose steam at high temperatures. The oxides $\overset{II}{R}O$ are all known and are 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 nickel, cobalt, iron and ruthenium of Group VIII form compounds called **carbonyls** with carbon monoxide. Molybdenum also forms a carbonyl.

The formulae of the carbonyls are:

$Ni(CO)_4$	$Fe(CO)_4$	$Ru(CO)_2$
$Co(CO)_3$	$Fe(CO)_5$	$Mo(CO)_6$
$Co_2(CO)_8$	$Fe_2(CO)_9$	or $Mo_5(CO)_{26}$.

IRON.

Iron.—The element iron, by reason both of its abundant occurrence and of its manifold uses, is undoubtedly the most important metal. Metallic iron was known in the Predynastic period in Egypt (before 3400 B.C.) but was exceedingly scarce and used only as beads for jewellery (Flinders Petrie). It may have been obtained from meteoric or native iron. The metal was 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. The metal came into general use in Egypt only much

later (about 1500 B.C.) and gradually displaced bronze, which was in use as early as 3000 B.C. The use of iron seems to have spread from the Hittites in Asia Minor. It was much used by the Assyrians about 600 B.C. The Etruscans worked the mines of Elba, later taken over by the Romans, who also worked the mines of Spain and Noricum. Iron seems to have been worked at an early date in India and in China.

Iron does not occur to any great extent in the free state on the earth, although meteorites, which sometimes consist of metallic iron with from 3 to 30 per cent of nickel, and some occluded hydrogen, indicate that it must be present in the solar system.

Meteorites may also consist partly or principally of silicates (*e.g.*, olivine) and of glassy minerals (moldavite), although grains of metallic iron are usually present even in the stony varieties On account of the presence of nickel, meteoric iron does not easily rust in moist air Cobalt, graphite, ferrous sulphide, and a peculiar mineral *schreibersite*, $(Fe,Ni,Co)_3P$, not known to exist on the earth, also occur in meteorites 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 Giants' Causeway and elsewhere. Iron compounds occur in the soil, in green plants, and in haematin (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. The most important ores are the oxides. The black oxide, Fe_3O_4, **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 *haematite*, which is sometimes 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 also occurs in earthy, granular and nodular forms and 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, France, Germany, 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 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.

The metallurgy of iron.—Three varieties of commercial iron are made: (1) **cast-iron**, or pig-iron; (2) **malleable iron**, or wrought-iron; (3) **steel**. The order in which they are prepared from the ore is roughly as follows:

Ore → Cast, or Pig-iron → Wrought-iron → Crucible Steel.
Cast, or Pig-iron → Bessemer, or Open-hearth Steel.

The extraction of iron from the ores 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 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, consists (Fig. 386) of an outer shell of steel plates, lined with refractory

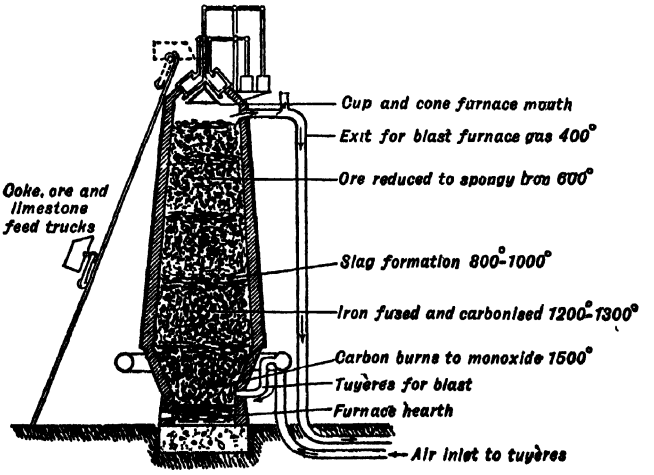


FIG. 386.—Blast furnace.

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* through

which a mixture of ore and fuel is fed intermittently into the furnace, whilst the gases (carbon monoxide and nitrogen) pass away through a pipe to a *dust-catcher*, and are utilised in heating the blast. The furnace below the boshes narrows gradually to a *hearth* 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 an annular pipe by means of powerful blowing engines The hearth is also pierced with a hole 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 3–5 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.

The first extensive use of cast-iron was in England in 1544. Formerly, charcoal was used as fuel; coal was first used by Dudley in England in 1619, but was afterwards given up until 1713, when coke was introduced by Darby at Coalbrookdale in Shropshire. Coal is still used in Scotch furnaces but elsewhere hard coke is employed

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 2½ tons) as produces 1 ton of iron The process is continuous and goes on day and night without interruption. The furnace should not be allowed to cool, when a hard mass of slag and metal would be produced Each furnace may produce 1000–1300 tons of cast-iron per week In America a higher production is sometimes attained by using a higher blast pressure.

The air blast has, since 1828, been pre-heated to 700°–800° by passing the air through **Cowper stoves** (Fig. 387) 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 tyueres is 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_2, 12; H_2 and CH_4, 4.

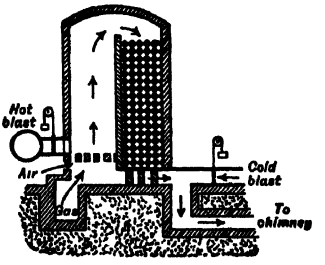


FIG 387.—Cowper stove.

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 at a very high temperature in the hearth to produce carbon monoxide $2C + O_2 \rightleftharpoons 2CO$. 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. Another reaction also occurs which limits the completeness of the reduction.

$$2Fe + 3CO \rightleftharpoons Fe_2O_3 + 3C.$$

In this upper zone the limestone is decomposed: $CaCO_3 \rightleftharpoons CaO + CO_2$, and some carbon dioxide is reduced to monoxide: $CO_2 + C \rightleftharpoons 2CO$. 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 · $2CO \rightleftharpoons CO_2 + C$ This and the carbon of the charge complete the reduction ·

$$Fe_2O_3 + 3C \rightleftharpoons 2Fe + 3CO$$

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 which usually contains some calcium sulphide, CaS.

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.

Cast-iron.—*Pig-iron* contains from 2·2 to 4·5 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 laminae 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 4·25 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 Henry Cort, of Lancaster, in 1783. The cast-iron is fused in a reverberatory furnace, the hearth of which is lined with haematite 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 below 1000°. 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 from 0·15 to 1·5 per cent. of combined carbon dissolved in the form of cementite, Fe_3C. Steel may be made (1) from cast-iron by removing part of the carbon, (2) from wrought-iron by adding combined carbon. Modern steel is produced by removing part of the carbon of cast-iron by:

(1) **The Bessemer process** (Henry Bessemer, 1855), or
(2) **The open-hearth process (Siemens-Martin process,** W. Siemens, 1863, and E. Martin, 1864).

If cast-iron is cast in a metal mould so as to cause rapid cooling, the cementite may be decomposed by heating the casting, embedded in haematite, for several days. The combined carbon in the surface is oxidised and that from the interior diffuses out to replace it. Finally

the carbon content is reduced to that of steel, and a *malleable casting* is produced In America the cementite in the interior is caused to decompose with separation of fine graphite and the iron becomes soft. The result is called a " black-heart casting," since it is white outside with a black core

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, although hydrocarbon gases, cyanogen and cyanides also cause cementation

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. 388), a large pear-shaped iron vessel lined with refractory silica bricks, The converter holds 10 tons of metal and is supported on trunnions, air being led by a pipe to a hollow perforated bottom, 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 now freely evolved from the molten iron and burns at the mouth of the converter as an orange-yellow flame edged with blue and 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-

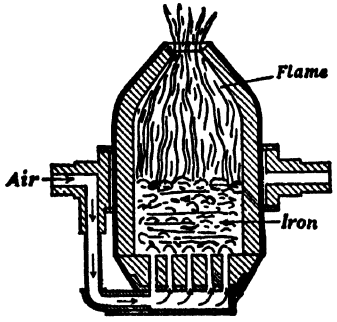


FIG 388.—Section of Bessemer converter

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 alloys of iron with manganese, tungsten, chromium, molybdenum, titanium, cobalt, nickel, and vanadium

Ores of iron containing phosphates give in the ordinary way cold-short iron. 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*), which is used as a 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.

The open-hearth process.—The open-hearth process is one of the few processes in the metallurgy of iron invented outside of England.

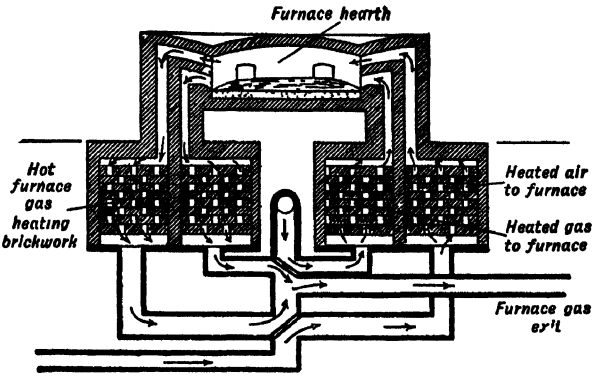


FIG. 389.—Open-hearth steel furnace.

It was suggested by Réaumur in France in 1722, and worked on the technical scale in 1864 by the brothers Martin in France, who made use of the regenerative heating process of Werner Siemens. It is carried out in a large flat crucible enclosed in a furnace (Fig. 389)

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. Molten cast-iron from the blast-furnace is run on the hearth. which is lined with silica in the acid process or calcined magnesite or dolomite in the basic process. The requisite amount of haematite, 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 a 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. Such furnaces are more especially used for the production of alloy steels, containing nickel, chromium, vanadium, and molybdenum.

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 of carbon. 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 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 900°, is soft, magnetic, and capable of dissolving but little iron carbide, Fe_3C. (2) **γ-Ferrite**, produced by heating above 900°, is non-magnetic, but differs from the other two varieties

in forming solid solutions with iron carbide. (3) At 1400°, δ-ferrite (which may be identical with α-ferrite) is formed:

$$\alpha\text{-ferrite} \overset{900^\circ}{\rightleftharpoons} \gamma\text{-ferrite} \overset{1400^\circ}{\rightleftharpoons} \delta\text{-ferrite.}$$

Iron loses its ferro-magnetism at about 760°, but this is not due to an allotropic change. α-iron and δ-iron have body-centred cubic lattices, whilst the γ-iron lattice is face-centred (see p. 430).

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 *austenite* (hard steel)

When the cooling is carried out *slowly*, decomposition of cementite may occur and solidification takes place at 1137° with production of a heterogeneous mass of iron and scales of graphite. The addition of manganese, nickel, etc., retards the conversion of γ-ferrite into α-ferrite, and thus produces a more homogeneous steel, the Fe_3C remaining in solution as austenite.

In Fig 390, *A* is the melting point (1533°) of pure iron (δ-ferrite); this is lowered by addition of carbon to the liquid metal as illustrated by the freezing point curve *AB* (*liquidus curve*) *AC* represents the lowering in melting point due to the solution of carbon in solid iron (*solidus curve*) Since the composition of the *solid* is now variable (solid solution), the curve *AE* of Fig. 348 is now replaced by two curves, *AB* and *AC*, one representing the solid, the other the liquid *B* is a eutectic point, 1125°, at which the molten mass solidifies to a mixture of cementite and austenite. The curves show that if the molten iron contains less than 2 per cent. of carbon it may solidify entirely to austenite. Cementite is deposited from alloys with more than 4·3 per cent. of carbon. *BD* is the solubility curve of cementite.

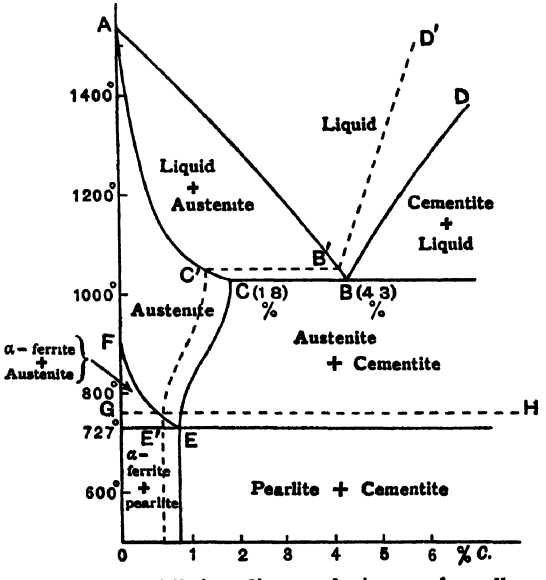


FIG. 390.—Equilibrium diagram for iron-carbon alloys. (Simplified near A)

On further cooling the solubility of carbon in γ-iron decreases and hence cementite is deposited from the *solid* mass, the percentage of combined carbon in the austenite decreasing This is shown by the curve *CE*, *E* corresponding with 0 89 per cent of carbon At 900°, however, γ-ferrite is converted into α-ferrite, which does not form a solid solution with carbon The carbon present in the γ-ferrite causes a depression in the transformation point γ-ferrite $\rightleftharpoons$ α-ferrite according to the curve *FE*. *E* is a eutectic point where the remaining austenite is converted into a mechanical mixture (*eutectoid*) of α-ferrite and cementite known as *pearlite*. Below 727° no further changes occur

It seems to have been fully established that the change at 760° formerly called $\alpha \rightarrow \beta$ is not a phase transformation but a magnetic transformation which, unlike an allotropic or phase transformation, does not take place at a definite temperature but is a progressive change, the velocity of which is a function of the temperature An allotropic form, β-ferrite, therefore does not exist. The magnetic transformation is represented by *GH* in the diagram. The thermal change taking place is the cause of *recalescence*, the sudden re-heating of a mass of red-hot iron on cooling

When graphite separates out in place of cementite, as sometimes happens when the cooling is very slow, the points *B*, *C* become *B'*, *C'*, respectively *B' D'* is the solubility curve of graphite, it intersects the curve *AB* at 1137°

The various 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

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 (obtained by heating recrystallised ferric nitrate) in hydrogen at 1000°, 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° with 180 amp. per sq. ft. of cathode. It is a soft almost white metal, sp. gr. 7·86, m. pt. 1533°, b. pt. 2450°. Iron is the most tenacious of all ductile metals except nickel and cobalt. It is permeated by hydrogen at 350°, the permeability increasing rapidly as the temperature rises to a red heat, and it burns brilliantly in oxygen when heated to redness. *Reduced iron* is a black or grey powder obtained by heating ferric oxide in hydrogen; when prepared from pure oxide (from the nitrate by reduction at a fairly low temperature) it is pyrophoric.

Iron readily occludes hydrogen, nitrogen and carbon monoxide, the solubility increasing with rise in temperature and showing a marked alteration about 936° The excess of gas is liberated on cooling the molten metal, and that retained by the solid is removed by heating in a vacuum

Iron on electrolysis (and therefore electrolytic iron) takes up hydrogen and becomes brittle the gas is expelled and the metal becomes soft on heating During the passage of hydrogen through heated iron or steel, the carbon, sulphur and phosphorus are removed as gaseous hydrides and the metal becomes soft

Iron does not easily amalgamate with mercury, but an amalgam is obtained by rubbing iron powder with mercuric chloride and water, or by the action of sodium amalgam on ferrous chloride solution . 1 per cent sodium amalgam gives 1 29 per cent iron amalgam

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 somewhat 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 or acidity 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 1.—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. 2.—Pour 100 c.c. of 15 per cent. caustic potash solution into a 500 c c flask fitted with a partly bored cork, and shake. Allow the flask to stand for two days Boil a large bright nail with distilled water as described above (*a*), 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. 3.—It will be noticed in Expt 1 (*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 Pack a number of bright nails tightly 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

Dunstan, Jowett and Golding (1905) assumed the reactions:

$$Fe + O_2 + H_2O = FeO + H_2O_2,$$
$$Fe + H_2O_2 = FeO + H_2O,$$
$$2FeO + H_2O_2 = 2FeO(OH).$$

They were unable to detect any H_2O_2 during rusting, but a *trace* is said to be formed by the action of iron amalgam on alkaline solutions (Schonbein, Wieland and Franke, 1929)

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 specific action of carbonic acid is not introduced except as an additional source of hydrogen ions. 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:

$$Fe + 2H^{\cdot} = Fe^{\cdot\cdot} + H_2;$$
$$4Fe^{\cdot\cdot} + O_2 + 2H_2O = 4Fe^{\cdot\cdot\cdot} + 4OH';$$
$$Fe^{\cdot\cdot\cdot} + 3OH' = Fe(OH)_3$$

EXPT. 4.—Prepare a 1½ per cent. solution of agar-agar in hot water, 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 alkali formed. The cause of rusting on this theory is electrolytic and due to the different solution pressures 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 them 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 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 ordinary 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, and it is possible to dissolve out the iron, leaving the transparent skin of oxide, by anodic electrolysis in salt solution.

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**: $Fe + 2H^{\cdot} = Fe^{\cdot\cdot} + H_2$. In cold dilute nitric acid no gas is evolved, but the acid is reduced and ferrous nitrate with ammonium nitrate formed:

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + 2NH_4NO_3 + 3H_2O.$$

In warm dilute nitric acid iron dissolves to form ferric nitrate with evolution of nitric oxide:

$$Fe + 4HNO_3 = Fe(NO_3)_3 + NO + 2H_2O.$$

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 (see p 971).

The ferrous ion is readily oxidised to the **ferric ion**, $Fe^{\cdot\cdot\cdot}$, which is almost colourless, the yellow, 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. (iii) Ferrous salts are also oxidised by boiling with nitric acid or *aqua regia*:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O;$$
$$2FeCl_2 + Cl_2 = 2FeCl_3$$

Ferric salts are reduced to ferrous salts (i) by nascent hydrogen in acid solution, say by zinc and hydrochloric acid: $2Fe^{\cdot\cdot\cdot} + H_2 = 2Fe^{\cdot\cdot} + 2H^{\cdot}$; (ii) by hydrogen sulphide. $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$; (iii) by sulphur dioxide: $2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl$; or (iv) by stannous chloride: $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

A solution of silver nitrate oxidises a ferrous salt, silver being precipitated In this case a transfer of ionic charge occurs: $Fe^{\cdot\cdot} + Ag^{\cdot} = Fe^{\cdot\cdot\cdot} + Ag$.

Ferrous Salts.

Ferrous chloride.—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 is obtained in white lustrous scales on heating iron in a stream of hydrogen chloride: $Fe + 2HCl = FeCl_2 + H_2$, or by heating ferric chloride in hydrogen. $2FeCl_3 + H_2 = 2FeCl_2 + 2HCl$.

Expt 5.—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 formation of ferrous chloride

Anhydrous $FeCl_2$ is also obtained by adding NH_4Cl to $FeCl_3$ solution, evaporating and heating the residue in absence of air till all the ammonium salt has volatilised.

Anhydrous ferrous chloride is soluble in alcohol and ether. It volatilises at about 1000° and the 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 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 from the elements, 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**. $Fe_3(OH)_8$ or $Fe(OH)_2,Fe_2O_3$: $Fe_3I_8 + 8KOH = Fe_3(OH)_8 + 8KI$. This reaction is used in the preparation of potassium iodide.

Ferrous sulphate.—This is the most important ferrous salt and is obtained by dissolving iron in dilute sulphuric acid or by the slow oxidation of marcasite, or " coal-brasses," FeS_2, by air in presence of water (*pyrites* is stable in air, unless it is first roasted) The common form is *green vitriol*, $FeSO_4,7H_2O$, crystallising in monoclinic crystals isomorphous with one form of Epsom salt, $MgSO_4,7H_2O$ 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, $FeSO_4$. On heating, this gives a basic salt at 167°–480°; at a red heat it decomposes: $2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$. Crystalline hydrates of ferrous sulphate 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 to saturation in separate amounts of warm 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.

Iron dissolves in sulphurous acid without evolution of gas. the solution deposits colourless crystals of **ferrous sulphite**, leaving a solution of **ferrous thiosulphate** $2Fe + 3H_2SO_3 = FeSO_3 + FeS_2O_3 + 3H_2O$

Ferrous carbonate.—This compound occurs as *siderite* or *spathic iron ore* in rhombohedra isomorphous with calcite. It is formed on addition of an alkali carbonate to ferrous salts as a white precipitate, rapidly becoming 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 springs. 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.—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. It crystallises from strong caustic soda solution in flat green prisms, and is a definite compound. The precipitate rapidly becomes green in the air from formation of $Fe_3(OH)_8$, and finally brown, forming $Fe(OH)_3$. It reduces nitrates and nitrites to ammonia.

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, or a little sodium hyposulphite ($Na_2S_2O_4$) is added.

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 1377°. A mixture of FeO and finely-divided iron which is pyrophoric is obtained by heating ferrous oxalate at 150°–169° 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 oxide.—If ammonium chloride and ammonia are added to a solution of a ferric salt, a reddish-brown gelatinous precipitate of **ferric hydroxide** 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, adsorbs many substances strongly, and dries to a gum-like mass of indefinite composition. Crystalline hydrated ferric oxides occur in the minerals *limonite*, $2Fe_2O_3,3H_2O$, *gothite* and *lepidocrocite* (magnetic), Fe_2O_3,H_2O, and *hydrohaematite*, $2Fe_2O_3,H_2O$.

Substances of this composition are also formed from the gelatinous hydroxide under 5000 atm pressure at 30°–42·5°, 42·5°–62·5°, and above 62·5°, respectively (Ruff, 1901).

On ignition of the hydroxide, 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*).

The stable crystalline form of ferric oxide is steel grey but gives a red powder. All varieties become brown to dark violet at 650°–1000°, above this temperature they turn bluish-black or black, but when mixed with alumina, Fe_2O_3 becomes *yellow* on ignition

Colloidal ferric oxide 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 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.

Ferric oxide has feebly acidic properties 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 old **Löwig process** for the manufacture of caustic soda.

Ferroso-ferric oxide.—This oxide is strongly magnetic and is formed by heating iron to redness in air ("smithy scales") or in steam, or by heating ferric oxide in the electric furnace. The pure oxide is obtained as a black power 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**, $Fe_3(OH)_8$, or $Fe(OH)_2,Fe_2O_3$, formed as a black precipitate by adding caustic soda to a mixture of a ferrous and a ferric salt, is magnetic. 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 may be ferrous ferrite, $Fe:(FeO_2)_2$.

Ferric chloride.—This is the most important ferric salt. It is obtained anhydrous, in iron-black crystals with a green iridescence, on heating iron or (at 900°–1000°) ferric oxide in chlorine. The crystals volatilise at 280°, 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 with further rise in temperature, probably owing to dissociation:

$$Fe_2Cl_6 \rightleftharpoons 2FeCl_3 \rightleftharpoons 2FeCl_2 + Cl_2.$$

Temperature	-	448°	518°	606°	750°	1050°	1300°
Δ (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 $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$. 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. The **bromide**, $FeBr_3$, is formed similarly to the chloride, but the iodide does not appear to exist.

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 in solution. It is used in the separation of phosphates in qualitative analysis (p. 622).

Ferric sulphate.—A solution of this salt is obtained by boiling ferrous sulphate with sulphuric and nitric acids. Nearly pure nitric oxide is evolved: $6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$. A black solution containing $FeSO_4 \cdot NO$ (p. 577) 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 being measured. Prolonged boiling, preferably under reduced pressure, is necessary to complete the reaction.

Ferric sulphate is most easily obtained 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 brown-red owing to hydrolysis, but becomes paler on addition of sulphuric acid. With potassium and ammonium sulphates ferric sulphate forms **iron alums**, *e g*, $(NH_4)_2SO_4,Fe_2^{III}(SO_4)_3,24H_2O$, with a violet colour when pure but often pale yellow owing to the presence of ferric oxide 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, or in *warm* dilute nitric acid $Fe + 4HNO_3 = Fe(NO_3)_3 + NO + 2H_2O$, the dark brown solution (used as a mordant) deposits colourless cubic crystals of $Fe(NO_3)_3,6H_2O$, or monoclinic crystals of $Fe(NO_3)_3,9H_2O$

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°, f. 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 is passed through iron pipes or coal gas is stored under pressure in iron cylinders. Such gas deposits Fe_2O_3 on incandescent mantles in gas-burners. (On the metal carbonyls see Mond, *J. Soc. Chem Ind.*, 1930.)

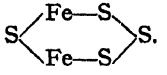
Sulphides of iron.—**Ferrous sulphide**, FeS, is formed as a black mass by heating 3 parts of iron filings with 2 parts of sulphur, a considerable amount of heat being evolved. It may be prepared by dipping a white-hot bar of wrought-iron into molten sulphur in a crucible. (Cast iron is not attacked.) 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 1170°. 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 hydrogen sulphide. A greenish-black precipitate of ferrous sulphide is formed when ammonium sulphide is added to a ferrous salt: $(NH_4)_2S + FeSO_4 = FeS + (NH_4)_2SO_4$, or hydrogen sulphide is passed through ferrous sulphate solution containing sodium acetate. The precipitate dissolves slightly in excess of yellow ammonium sulphide forming a dark greenish-black solution, probably containing a **ferrisulphide**, $(NH_4)FeS_2$, or $(NH_4)_2S,Fe_2S_3$.

Potassium ferrisulphide, $KFeS_2$, 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. It is removed and the soda liquor decolorised, by heating with zinc oxide, when Fe_2O_3 is precipitated and white ZnS is formed

Iron sesquisulphide, Fe_2S_3, is formed as a yellow mass with a metallic lustre by gently heating iron with sulphur, by heating ferric oxide in H_2S below 100°, or by the action of H_2S on moist ferric hydroxide in absence of alkali 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 source of much 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*.

FeS_2 is formed by gently heating FeS with sulphur, by passing H_2S over iron oxides or chlorides heated to redness, or by heating a mixture of Fe_2O_3, sulphur and NH_4Cl It is supposed to contain ferrous iron.



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** (sometimes called perferrate), K_2FeO_4, is deposited. On boiling, a yellow solution of **potassium ferrite** (sometimes called ferrate), $K_2Fe_2O_4$, 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.—No simple cyanides of iron are known; if potassium cyanide is added to a solution of ferric chloride, hydrocyanic acid is evolved and ferric hydroxide is precipitated $FeCl_3 + 3KCN + 3H_2O = Fe(OH)_3 + 3HCN + 3KCl$ 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, **hydroferrocyanic 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 ferrous iron, $4KCN,Fe(CN)_2$, but it is now regarded as the potassium salt of the complex hydroferrocyanic 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 prepared from the spent-oxide of gas works by mixing with lime, heating, dissolving out the calcium ferrocyanide, precipitating $CaK_2Fe(CN)_6$ with KCl and decomposing this with K_2CO_3 The nitrogen of the coal is partly evolved as hydrocyanic acid, 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, it is said, 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.—If chlorine is passed through a solution of potassium ferrocyanide, the quadrivalent ferrocyanide ion, $\overset{II}{Fe}(CN)_6''''$, is *oxidised* 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 $4Fe(CN)_6''' + 2Cr''' + 10OH' = 4Fe(CN)_6'''' + 2CrO_4'' + 5H_2O$), and it evolves chlorine when heated with concentrated hydrochloric acid. 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 **Sodium ferricyanide**, $2Na_3Fe(CN)_6,H_2O$, is obtained from sodium ferrocyanide and chlorine.

Hydroferricyanic 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**, $\overset{II}{K_2}\overset{II}{Fe}(FeCy_6)$, is formed, which rapidly oxidises in air to **β-soluble Prussian blue** or potassium ferric ferrocyanide, $\overset{III}{Fe}\overset{II}{K}(FeCy_6),H_2O$, 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 is evolved $2K_4FeCy_6 + 3H_2SO_4 = 3K_2SO_4 + \overset{II}{K_2}\overset{II}{Fe}(FeCy_6) + 6HCN$ The pale yellow powder, $K_2Fe(FeCy_6)$, 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**, $\overset{III}{K}\overset{II}{Fe}(FeCy_6),H_2O$

By heating a solution of hydroferrocyanic acid at 110°–120° in a sealed tube a precipitate of the acid corresponding with the white precipitates, viz ferrous hydrogen ferrocyanide, $\overset{II}{H_2}\overset{II}{Fe}(FeCy_6)$, is formed, which on oxidation gives a violet compound, possibly $\overset{III}{H}\overset{II}{Fe}(FeCy_6)$.

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, then with 70 per cent. alcohol, and dried over P_2O_5, it forms **α-soluble Prussian blue** or **α-ferric potassium ferrocyanide**, $4\overset{III}{Fe}\overset{II}{K}(FeCy_6),7H_2O$ 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.

α-soluble Prussian blue may have the formulae: $\overset{III}{Fe}\overset{II}{K}(FeCy_6)$ or $\overset{II}{Fe}\overset{III}{K}(FeCy_6)$. 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 $\overset{III}{Fe}_4\overset{II}{(FeCy_6)_3}$ or Fe_7Cy_{18}, but contains water which cannot be driven off

by heat, and is generally formulated as $Fe_7Cy_{18},9H_2O$. It is the main constituent of 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, $\overset{II}{Fe_3}(\overset{III}{FeCy_6})_2$, 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, when 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 $\overset{III}{Fe}(\overset{III}{FeCy_6})$, is formed

The above account of the cyanogen compounds of iron is based on the researches of K A Hofmann, other formulae have also been proposed

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 probably due to the formation of $Na_3\overset{III}{Fe}(O\cdot N\,SNa)Cy_5$, with alkali-sulphides but not with free hydrogen sulphide 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. A salt is also formed by passing nitric oxide into acidified solution of potassium ferricyanide: $K_3Fe(CN)_6 + NO = K_2[Fe(NO)(CN)_5] + KCN$ The NO in these compounds is not the nitroso-radical —NO, but the neutral molecule.

Ferric thiocyanate —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 $FeCl_3 + 3KCNS \rightleftharpoons Fe(CNS)_3 + 3KCl$ If the solution is shaken with ether, the latter dissolves the ferric thiocyanate. 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, colourless in solution The red colour of the ferric salt is due to the undissociated molecules

Peculiar 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, or 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 alkali sulphides, or ferrous sulphate acts on a mixture of nitrite and sulphide of an alkali, black compounds (**Roussin's salts**) are formed, *e g* , $KFe(NO)_2S$ and $KFe_4(NO)_7S_3$, 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

CHAPTER L

COBALT AND NICKEL

Cobalt.

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 a mischievous spirit, *kobold* (the Greek κόβαλος), and the material was called "false-ore," or *cobalt*.

The use of cobalt as a constituent of some blue glazes and blue glass, made in imitation of lapis lazuli (p 828), has been established for ancient Egyptian (1375 B C) and Babylonian (about 1450 B C) specimens by analysis Most of the ancient blue glazes, however, owe their colour to a compound of copper, $CuO,CaO,4SiO_2$ Some specimens of Roman blue glass (*e g.*, a piece found at Uriconium), owe their colour to cobalt

The roasted *cobalt*, called *zaffre* (impure cobalt arsenate), gave 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 glass windows of the mediaeval 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, $CoAs_2$), known as *speiss cobalt* or *smaltite* A similar ore is *linnaeite*, $(Co,Ni,Fe)_3S_4$ 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 arsenides and sulphides in the silver ores of Cobalt City, Ontario, and from New Caledonia, where manganese ore containing about 2 per cent. of cobalt oxide occurs.

Metallurgy of cobalt.—The ore is roasted to free it from some arsenic and sulphur, and fused in a blast-furnace with limestone and sand as a flux. The iron passes into the slag and impure arsenide and antimonide of nickel and cobalt (*speiss*) settles out. This is ground, roasted to drive off most of the arsenic (and antimony, if present), and then

roasted with salt If silver is present it is extracted by cyanide The residue is boiled with concentrated sulphuric acid and the " sulphated speiss " agitated with water, the iron, arsenic and antimony are precipitated with limestone, copper from the filtrate by sodium carbonate, and the cobalt is thrown down by sodium hypochlorite, which precipitates cobalt peroxide. Finally, nickel is precipitated from the filtrate as basic carbonate by adding sodium carbonate, the last portions being thrown out as peroxide by adding a little hypochlorite

The cobalt and nickel oxides are sold as such, or reduced by heating in an electric furnace with carbon and limestone. The metal usually contains about 1 per cent of carbon and 0·015 per cent of sulphur The calcined cobalt oxide contains less than 1 per cent of nickel and 71–75 per cent of cobalt The metal may also be prepared by the electrolysis of a solution of the sulphate, $CoSO_4$, containing ammonium sulphate and ammonia

Cobalt is tenacious, silver-white in colour with a slight bluish cast which nickel has not, is readily polished and shows a high lustre. Its specific gravity is 8·8, it is magnetic up to 1100°, and melts at 1444° or 1480°. 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 steel (35 per cent Co) is used for permanent magnets for magnetos, as these can be made much smaller than carbon steel magnets, retain their magnetism much more tenaciously and do not tend to become demagnetised *Stellite* is an alloy of chromium, tungsten and cobalt, very hard and non-corroding, used for surgical instruments. *Festel metal* is an alloy of cobalt, iron and chromium used for cutlery

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 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 is thrown down, which on standing, more rapidly on boiling, is converted into a pink basic salt or impure cobaltous hydroxide, $Co(OH)_2$.

The colour changes are due to structural changes in the precipitate and reflection of light from laminae, the actual substance is yellowish-green.

When heated out of contact with air the hydroxide forms an olive-green powder of the basic **cobaltous oxide**, CoO. Cobaltous hydroxide dissolves only in traces in excess of caustic potash but the precipitate from a cobalt salt is soluble in excess of 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. 985).

On gently igniting cobalt nitrate a **sesquioxide**, Co_2O_3, is obtained as a dark brown powder. The oxide formed on addition of bleaching-powder, or iodine and caustic potash, to a solution of a cobaltous salt is the **dioxide**, CoO_2 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.

When hydrogen peroxide is added to cobaltous hydroxide suspended in water, the filtrate is acid and becomes green on addition of potassium hydrogen carbonate Cobaltous acid, H_2CoO_3, or a complex cobalt compound, $[\overset{III}{Co}(KCO_3)_2]_2O$, or a compound $CoCO_3,Co_2O_3$, may be formed

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 blue borax bead

Cobalt salts.—The ordinary salts contain bivalent (**cobaltous**) cobalt. Tervalent (**cobaltic**) cobalt salts are usually rather unstable (although the complex compounds are very stable), and include the oxide Co_2O_3, sulphide Co_2S_3, the green fluoride CoF_3 obtained by electrolytic oxidation, and the blue sulphate $Co_2(SO_4)_3$, $18H_2O$, also obtained by electrolytic oxidation, forming an unstable alum, and a powerful oxidising agent

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 hydrate $CoCl_2,H_2O$, obtained by heating, are 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 hydrogen sulphide The latter is the original invisible ink (N. Lemery, 1681). The cobalt ink was introduced in 1705.

The pink solutions of cobalt chloride become blue on heating or addition of concentrated hydrochloric or sulphuric acid, and the solid gives a bluish-purple solution with alcohol. A complex blue anion, $CoCl_4''$, appears to be formed: $2CoCl_2 \rightleftharpoons Co'' + CoCl_4''$. Cobalt nitrate solution becomes blue when concentrated hydrochloric acid is added, but not with sulphuric acid

Cobaltous sulphate, $CoSO_4,7H_2O$, is isomorphous with $NiSO_4,7H_2O$ and $FeSO_4,7H_2O$. It crystallises with different amounts of water according to the temperature; the solution at 40°–50° deposits $CoSO_4,6H_2O$, isomorphous with $ZnSO_4,6H_2O$, and when poured into concentrated sulphuric acid it gives $CoSO_4,4H_2O$. The anhydrous salt is rose-red. Double sulphates, *e.g.*, $K_2SO_4,CoSO_4,6H_2O$, are known

Cobalt sulphide, CoS, is precipitated by ammonium sulphide or by hydrogen sulphide in presence of sodium acetate It is black and although not precipitated by hydrogen sulphide from acid solutions, it is insoluble in dilute acids but is soluble in concentrated hydrochloric acid and *aqua regia*.

A **persulphide**, possibly Co_2S_7, is formed as a black precipitate with sodium sulphide saturated with sulphur **Cobaltous carbonate**, $CoCO_3$, $6H_2O$, is formed as a pink precipitate on addition of bicarbonates to cobalt salts and allowing to stand, it gives a pink double salt with potassium carbonate and a bright reddish-purple one with sodium carbonate, with the formula $M_2CO_3,CoCO_3,4H_2O$. **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, perhaps formed at high temperatures, is 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 reddish-brown precipitate of **cobaltous cyanide**, $Co(CN)_2,3H_2O$, is thrown down. This dissolves in excess of cyanide forming a yellow solution of **potassium cobaltocyanide**, $K_4\overset{II}{Co}(CN)_6$, analogus 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: thus $2K_4Co(CN)_6 + H_2O + O = 2K_3Co(CN)_6 + 2KOH$. 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 white precipitate Ag_3CoCy_6, with silver nitrate, and a blue precipitate $Cu_3(CoCy_6)_2$, with copper sulphate, 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 a cobaltous salt acidified with acetic acid a yellow precipitate of **potassium cobaltinitrite**, $K_3Co(NO_2)_6$ (*Fischer's salt*), only slightly soluble in water: $CoCl_2 + 5KNO_2 + 2HNO_2 = K_3Co(NO_2)_6 + 2KCl + NO + H_2O$ 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 $K_3Co(NO_2)_6$, 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 α-nitroso-β-naphthol dissolved in acetic acid gives the cobalt salts a red precipitate; it does not precipitate nickel salts

On addition of excess of ammonia to a cobalt salt and exposure to air, absorption of oxygen occurs and a brown solution is formed which becomes pink on boiling. The solutions contain complex **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 reaction occurs more rapidly if lead dioxide is added.

NICKEL.

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 1751, Cronstedt obtained impure metallic nickel from this ore, the properties of the element being investigated more thoroughly by Bergman in 1774. A coin of the Bactrian king Euthydemos (235 B.C.) contains 77·58 per cent. of copper and 20·04 per cent. of nickel, and alloys of copper, zinc and nickel seem to have been used in China before this date.

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, $(Ni,Mg)SiO_3,xH_2O$, found in New Caledonia, and *pentlandite*, (Ni,Cu,Fe)S, or $(Ni,Fe)_{11}S_{10}$, containing about 2·5 per cent. of nickel, found at Sudbury, Ontario. *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 (the most important) are roasted, smelted with coke and bessemerised, yielding a *matte* containing 25–30 Cu, 56 Ni (sometimes with cobalt), 0·1–0·5 Fe and 14–17 S. This may be roasted and refined, and the copper and nickel oxides reduced by carbon in open hearth or electric furnaces to give *monel metal* containing 67 Ni, 28 Cu, and 5 of Mn and Fe, resembling nickel in colour and properties. If the *matte* 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. The top layer is bessemerised to copper, the lower layer is purified and is roasted to nickel oxide, NiO, and the latter reduced by heating strongly with charcoal powder. Garnierite is fused with gypsum and coke, and the matte blown in a converter or smelted in a reverberatory furnace with a siliceous flux. Iron is removed and the nickel sulphide is worked as before

Nickel is extracted from Canadian *matte* by the Mond carbonyl process, worked at Clydach in South Wales In this process (1895), the roasted *matte* is leached with sulphuric acid solution containing copper sulphate to remove copper, which is converted into blue vitriol. The residue is reduced at 300° 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 at the ordinary temperature down a tower provided with shelves and carbon monoxide is passed through, when volatile **nickel carbonyl**, $Ni(CO)_4$, is produced. This is passed through a decomposer heated at 150°. Decomposition occurs and metallic nickel is deposited on nickel granules kept stirred : $Ni(CO)_4 \rightleftharpoons Ni + 4CO$, the carbon monoxide passing back to the volatiliser. The metal is 99·8 per cent. pure , it contains 0·06 per cent. of iron, 0·09 per cent. of carbon and traces of sulphur and silicon

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 ; or by passing CO_2 and O_2 over heated carbon. Nickel may be cast a little magnesium may be added before casting to increase the fluidity and to remove gas-bubbles

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, and soon tarnishes in town air.

Metallic nickel is of a greyish-white colour, sp. gr. 8·35 (cast)—8·9 (rolled), m. pt. 1452°, very hard and malleable and capable of taking

a high polish. It is fairly resistant to pure air but gradually becomes dull and is rapidly covered with a dull film in air containing sulphur compounds or soot. It is rendered passive by nitric acid. Nickel is magnetic below 340°. At this temperature an allotropic change occurs. Finely-divided nickel absorbs 17 times its volume of hydrogen It decomposes steam at a red heat. $Ni + H_2O \rightleftharpoons NiO + H_2$. 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, and readily in dilute nitric acid, a green solution being obtained The colour is that of the nickel ion, $Ni^{\cdot\cdot}$, and is shown by all the simple salts of nickel On evaporation of the solution in nitric acid, green monoclinic crystals of the **nitrate** $Ni(NO_3)_2,6H_2O$ are deposited. By dissolving the oxide or carbonate in dilute sulphuric acid and evaporating, green rhombic prisms of **nickel sulphate** $NiSO_4,7H_2O$ separate, isomorphous with Epsom salt. 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 alkali throws down from solutions of nickel salts an apple-green precipitate of **nickel hydroxide**, $Ni(OH)_2$, insoluble in excess but somewhat soluble in ammonia, and soluble in ammonium salts forming a blue solution The **ammine salts** of *bivalent* nickel, *e.g.*, $Ni(NH_3)_6Cl_2$ and $Ni(NH_3)_4SO_4,2H_2O$, may be obtained in blue crystals On heating the hydroxide, **nickel monoxide** NiO is obtained as a green 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 produces H_2O_2 by the action of acids.

Nickel hydroxide is not oxidised by atmospheric oxygen (cf. ferrous and manganous hydroxides) or hydrogen peroxide, but sodium hypochlorite or hypobromite oxidises it to the dioxide, which can readily be filtered.

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, when it is much denser. It is insoluble in dilute acids but dissolves in warm *aqua regia.*

Although nickel sulphide is not precipitated by hydrogen sulphide in presence of dilute hydrochloric acid, the precipitate obtained in alkaline solution is insoluble in dilute acid It is supposed that three isomeric forms of the sulphide exist (Thiel and Gessner, 1914).

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 poisonous and explosive Nickel carbonyl is best prepared under pressure, say 100 atm., which is favourable to the carbonyl 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 chiefly in the manufacture of *nickel steel,* usually containing about 3 5 per cent of nickel, of nickel crucibles and tubes, and alloyed with 75 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 60 nickel, 15 iron and 14 chromium, melts at a high temperature and is used for electrical resistance heaters *German silver* is the alloy 5 copper, 2 nickel and 2 zinc A similar alloy has long been used in China under the name *pakfong.* Alloys used for resistance coils, etc., are: *platinoid:* 60Cu + 24Zn + 14Ni + 1 − 2W; *constantan*: 40Ni + 60Cu; and *rheostan*: 52Cu + 18Zn + 25Ni + 5Fe.

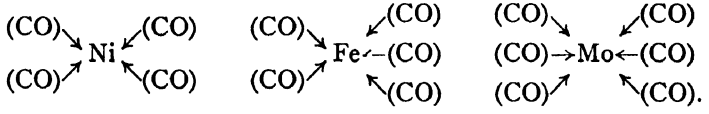
Separation of nickel and cobalt.—These two metals often occur together in analysis and their separation may be effected by the formation of a cobalticyanide, nickel forming only the bright red double salt, $Ni(CN)_2,2KCN$, or $K_2Ni(CN)_4,H_2O$, easily decomposed by acids, and from which hypochlorite precipitates black Ni_2O_3. This salt is reduced by sodium amalgam to a lower cyanide, possibly NiCN as $K_2Ni(CN)_3$. 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 α-nitroso-β-naphthol in glacial acetic acid gives a reddish-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, $(CN)_2(NH_2)_2$, and then caustic potash to an

acidified solution of a nickel salt. α-diphenylglyoxime is even more sensitive (1 of Ni in 10^6) than the methyl compound (0·01 mgm. Ni)

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 at 110°–120°, and weighed

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, liquids fats containing glycerol esters of unsaturated fatty acids such as oleic, if treated with pure hydrogen at 150°–250° in presence of a little suspended nickel oxide or oxalate, which are reduced, absorb hydrogen and form solid fats, *e g.*, stearin.

Electronic structures of the metal carbonyls.—According to Sidgwick the CO molecules in carbonyls are linked to the metal atom by co-ordinate links (semipolar double bonds), each CO donating a pair of electrons :



The effective atomic number (E A.N) of the metal, *i e.*, the number of electrons in and associated with the atom in the compound, is supposed to be equal to that of the inert gas at the end of the period 36(Kr) for Fe, Co and Ni, and 54(Xe) for Mo. The maximum number of additional electrons which can be accommodated in a covalent compound is the E A.N. minus the atomic number of the atom . for Ni $36-28=8$, for Co $36-27=9$, for Fe $36-26=10$, for Mo $54-42=12$. Thus the existence of $Ni(CO)_4$, $Fe(CO)_5$ and $Mo(CO)_6$ is explained (p 690).

CHAPTER LI

THE PLATINUM METALS

Platinum.—The hieroglyphs on an Egyptian box discovered at Thebes and dating from seventh century B C , were found by Berthelot to be composed of an alloy of platinum, iridium, and gold Scaliger (1557) says there was found in Mexican mines a metal " which no fire or art of the Spaniards can bring to liquefaction," and this metal is again mentioned by Don Antonio de Ulloa, who visited Mexico in 1735. Specimens of platinum were brought to Europe from Carthagena in 1741 by Charles Wood ; it was called by the Mexicans *platina de pinto*, and was examined by William Brownrigg in 1750, further by Lewis in 1754, by Marggraf in 1757, and by Bergman in 1777. Platinum foil and wire were first made in 1772 by Count von Sickingen, an ambassador in Paris, and in 1806 they were sold in London for chemical purposes at 16s an ounce

The deposits are in the Urals (discovered in 1823), California, Brazil, Borneo, and Australia, especially New South Wales Platinum metals in the nickel ores of Sudbury, Ontario (p 985), are extracted on an important scale as by-products in the Mond nickel process. Platinum occurs in several hard rocks in South Africa, but the native metal is usually obtained by washing alluvial sands and gravels The concentrates consist of metallic grains, which in a Russian specimen 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	55·2	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 at 125°. Palladium and rhodium form insoluble lower chlorides, $PdCl_2$ and $RhCl_3$. 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 soluble ammonium salt, $(NH_4)_2PtCl_6$. 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 oxyhydrogen flame.

Properties of platinum.—Platinum is a tin-white metal of high density, 21·4, and high melting point, 1755°. 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. Platinum is 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 It is said to be appreciably volatile at 1300°, or even at 800° when exposed to air. Platinum which gains in weight on heating contains iron 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, sulphides, and sodium peroxide also attack the metal in a fused state, and it is slightly attacked by the fused carbonates, but not by hydrofluoric acid Fused lithium and magnesium chlorides, potassium cyanide and nitrates, 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." The product may contain $Pt(NO)_2Cl_6$.

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, by copper coated with boron trioxide, or Eldred's wire, which has a core of nickel steel, a jacket of copper and an outer sheath of platinum or a fused film of potassium borate. Platinum is used in dentistry and in making jewellery, especially as a

setting for diamonds It is used for contacts in electrical apparatus, and 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 to aldehyde by platinum black, on account of its occluded oxygen, and a mixture of oxygen and hydrogen is exploded by platinum sponge or even by very clean foil.

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. 1 —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. The acid 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 there.

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 on heating.

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 390° in chlorine, the greenish-black **trichloride,** $PtCl_3$, is obtained, and at 580°, brownish-green **platinum dichloride,** $PtCl_2$.

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 sulphur dioxide on chloroplatinic acid solution

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 acetate 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, $K_2O,3PtO_3$, is 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 plantinochloride**, 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").

Hydrogen sulphide 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 chloroplatinate, 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 combined with the metal atom as in the cobaltammines (p. 985); 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 is warmed and treated with sulphur dioxide till colourless $BaSO_4$ is filtered off and the filtrate crystallised

Palladium.—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, but this is reduced again at a higher temperature. 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.

Osmium and Iridium.—These two metals are contained in osmiridium (p. 990) If this is fused with sodium chloride in a current of 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, m pt 39 5° and 41° (2 forms), b pt 130°, 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 OsO_4 forms very unstable salts with strong alkalies, *e g*, $OsO_4,2KOH$ The fluoride OsF_8 is known

Ruthenium and Rhodium.—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 $(NH_4)_2RuO_5$ is known

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).

QUESTIONS

CHAPTER I

1. 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

2 Explain what is meant by the terms phase, heterogeneous, homogeneous, colloidal solution, precipitate

3 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 ?

4 How are (*a*) flotation, (*b*) electrostatic precipitation, (*c*) electromagnetic separation, applied on the large scale ?

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 ?

4. According to Lavoisier, " in all the operations of art and nature, nothing is created an equal quantity of matter exists before and after the experiment." What is meant by this statement ? Describe any two experiments which support it (Joint Matric. Board School Cert)

CHAPTERS III-IV

1 Give an *historical* account of the discovery of the composition of air (London Inter.)

2. 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

3. Write a short essay on *one* of the following :
   (*a*) The Theory of Phlogiston.
   (*b*) Mayow's work on combustion and respiration.
   (*c*) The development of the Law of Mass Action.
   (London Inter. B.Sc)

4. Give a brief account of the discovery of oxygen (Mysore Inter.)

5 Describe carefully Lavoisier's experiments on the composition of air, and the inference he drew Describe any laboratory experiments you have performed to the same effect. (Calcutta Inter)

6 Write a historical account of the discovery of the composition of water (London Inter)

7 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 ?

8 Describe Dumas' experiments on the composition of water, and point out any experimental errors involved

9 Give a short historical account of the methods which have been used to determine accurately the proportions by weight in which hydrogen and oxygen combine (London Inter)

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 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

5 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 . (1) the weight of 1 cu. m. of the moist air ; (11) the humidity

6. 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 ?

7. Describe Victor Meyer's method for the determination of the vapour density of a liquid

In an experiment 0·4068 gram of liquid gave 45·3 c c. of air at 15° and 740 mm. Find the vapour density.

[1 c c. hydrogen at 0° and 760 mm. weighs 0·00009 gram.]
(London B.Com.)

8. State the law connecting the volume of a given mass of gas, *e g.*, oxygen, with (*a*) its pressure, (*b*) its temperature, and hence derive the usual gas equation connecting p, v and T. If the given mass of oxygen occupies 22·4 litres at 0° C. and 1 atmosphere pressure, what will be the gas equation in this particular case ? Use this equation to calculate the volume of the given mass of oxygen at 91° C. and at a pressure of 0·8 atmosphere. (Bombay B.A.)

9 The following quantities of gas are contained over mercury in separate measuring vessels 70·0 c c of hydrogen at 15° C and 720 mm , 10·0 c.c. of oxygen at 10° C. and 700 mm , 14·0 c c of nitrogen at 20° C. and 760 mm. All are mixed in another vessel at 18° C and the volume is found to be 94·0 c c What is the total pressure in the vessel and the partial pressure of each constituent ? (Bombay B.A)

CHAPTER VI

1. 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	1·43	1·33	1·17	1·01	0·85	0·72

2 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 ?

3 The absorption coefficient of carbon dioxide in alcohol at 0° C is 2·706 at a pressure of one atmosphere Calculate the weight of carbon dioxide dissolved by ten litres of alcohol under a pressure of three atmospheres at the same temperature (London Inter. B Sc)

4 State the laws which regulate (*a*) the quantities of the different constituents of a gas mixture, *e g* , air, dissolved when it is shaken up with a solvent, (*b*) the distribution of a soluble solid between two non-miscible solvents Given that the solubilities of iodine in water and carbon bisulphide are respectively 1 to 590 and that the molecular condition of the iodine is the same in each, what will be the weight of iodine left in 1 litre of an aqueous iodine solution, originally saturated at 18° C , after having been shaken with 100 c c of carbon bisulphide ? (Solubility of iodine at 18° C = 1 gram in 3616 c c of water) (London B Sc.)

5 State in as few words as possible the Gibbs's Phase Rule Enumerate the number of phases and components in each of the following systems (*a*) Freezing water (*b*) Water above 0° C (*c*) Sodium chloride and water. (*d*) Saturated solution of sodium sulphate at the transition point (Punjab B A)

6 Explain what is meant by the distribution law for a substance between two immiscible solvents Show its relationship to Henry's Law regarding a gas in solution Succinic acid was shaken up with water and ether. By titration, 10 c c. of the water solution and 10 c c. of the ether solution were found to contain respectively 0·854 gram and 0·159 gram of succinic acid In another experiment 1·0 gram of succinic acid was shaken up with 10 c.c. of water and 20 c.c. of ether. Calculate the weight of succinic acid dissolved in the water and in the ether respectively. (Bombay B.A.)

7. State the phase rule and explain clearly the terms involved. Apply the rule to the case of (i) sulphur, (ii) solution of sodium chloride in water (Bombay B.A.)

CHAPTERS VII-VIII

1 Give a short account of the nature and results of the controversy between Proust and Berthollet What difficulty remained for Proust to explain after his work, and what account did he give of it ?

2 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

3 150 000 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)

4. Write a short account of methods for determining the chemical equivalent of an element, and discuss in detail *one* such method

One gm of the chloride of a metal dissolved in water was mixed with an excess of silver nitrate solution The weight of the dried precipitate of silver chloride was 2·110 gm What was the equivalent of the metal ? (Ag = 107·88 , Cl = 35·46) (London Inter. B Sc)

5 Stas found that 1·0 gram of carbon yielded 3·7 grams of carbon dioxide When the lower oxide of carbon was passed over heated copper oxide, he found that 61·9 grams of carbon dioxide were formed and that the diminution in weight of the copper oxide was 22·5 grams Deduce the percentage composition of the lower oxide and show that the results are in agreement with the law of multiple proportions (Madras Inter)

6 What is meant by a pure substance ? A bottle labelled lead oxide contains a brown powder which on reduction is found to give 84 per cent. by weight of metallic lead Is this powder a pure substance ? (Pb = 207 , O = 16) (Madras Inter)

7 Discuss with examples the advantages of modern methods of atomic weight determination as compared with the methods used at the time of Stas (London B Sc)

8 State the law of Multiple Proportions By means of the following analytical results show that this law is true

Mercurous Chloride	Mercuric Chloride
Mercury = 84·92%	Mercury = 73·80%
Chlorine = 15·08	Chlorine = 26·20
100 00	100·00

(London Inter. Coll. Schol. Board)

9 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 32 gm. of oxygen at S T P occupy 22·4 litres find the weight of barium peroxide required to make 10 litres of oxygen, measured at 15° and 740 mm

10. 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 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.

11 What weights of crystallised potassium ferrocyanide, concentrated sulphuric acid (sp. gr. 1·84) and water are required to prepare 100 gm of carbon monoxide (p. 689) ? Sulphuric acid of sp gr. 1·84 contains 99·2 per cent of H_2SO_4

12 State the laws of chemical combination relating to weight, and explain carefully how they may be deduced from the atomic theory What is known of the degree of exactness of these laws ?

(London Inter B Sc)

13 State Dalton's atomic theory and show how the laws of definite and multiple proportions are deducible from it (Calcutta Inter)

CHAPTER IX

1 What weight of barium peroxide must be decomposed by heating to give 42 litres of oxygen at 18° and 740 mm ?

2 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 ?

3. 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, and explain why these are not exactly equal to 22 415 litres

4. 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

5. One gram of a metal set free from an acid 197·3 c c of hydrogen measured at 15° and 765 mm Calculate the equivalent

What further data are necessary in order to fix the atomic weight ? (1 litre of hydrogen at S T P. weighs 0·09 gram.) (Inter B Sc Wales.)

[*Note* —The molecular volume 22·4 litres corresponds exactly with 2 016/22 4 = 0 09 gm /lit of hydrogen, so that either is used in examination questions the *exact* figures are 2 0156 and 22 415, these give 0 08992 gm /lit , Morley's figure being 0 08987 gm /lit]

6. What is meant by the terms (*a*) acid salt, (*b*) basic salt, (*c*) thermal dissociation, (*d*) endothermic reaction, (*e*) amphoteric oxide, (*f*) strong base ? Give illustrative examples (London B Com.)

7 The vapour density of the chloride of a metal is 81·5 (H = 1). The chloride contains 34·46 per cent. of metal. The specific heat of the metal is 0·115. Find the *exact* atomic weight of the metal and the formula of the chloride (London Inter. Coll Schol Board)

8 State Gay-Lussac's law of gaseous volumes and Avogadro's hypothesis. How is the latter used in molecular weight determinations ? A quantity of gas weighing 0·062 gram occupies 25·64 c c. at 100° C. and 741 mm. pressure Calculate the molecular weight of the gas.

(Allahabad Inter.)

9. At 200° C. and 1 atm. pressure the vapour density (H = 1) of phosphorus pentachloride is 70. Calculate the percentage dissociation and the partial pressures of the substances present when 1 mol of PCl_5 is taken

10 Two oxides of a metal contain 36·8 and 30·38 per cent of oxygen. The specific heat of the metal is 0·117. Assign formulae to the two oxides (Bombay Inter. B Sc)

11 State the law of atomic heats defined by Dulong and Petit. 0·91 gram of the sulphide of a metal when roasted in air produced 263·5 c c. of sulphur dioxide at 27° and 710 mm pressure. The specific heat of the metal was found to be 0·0533 Ascertain the atomic weight of the metal. (Bombay Inter. B.Sc)

12. By means of a porcelain Victor Meyer apparatus 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.

13. Explain why the formation of hydrogen chloride from its elements is represented by the equation $H_2 + Cl_2 = 2HCl$ rather than by the equation $H + Cl = HCl$ (Joint Matric Board School Cert)

14 Explain how the molecular weight of a compound, obtainable in the gaseous state, can be ascertained? Why is the result false for ammonium chloride? When an element forms a sufficient number of volatile compounds, how may its approximate atomic weight be found? Describe how the result found may be checked, and, lastly, the exact atomic weight determined (Aberdeen First B Sc.)

15 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 (O = 16, Cl = 35·46). (London B.Sc)

16 Guye found that the weight of a normal litre of the gas obtained by the decomposition of ammonia was 0·3799 gram

Taking the weight of a normal litre of hydrogen as 0·0899 gram, and the weight of a normal litre of nitrogen as 1·2507 gram, then

(i) On the assumption that the gases obey Boyle's law, calculate the combining volumes of nitrogen and hydrogen at 0° C and the atomic weight of nitrogen.

(ii) If owing to deviations from Boyle's law the litre of nitrogen at 0° C. became 1·0004 litres when diluted with the 3 volumes of hydrogen, and the litre of hydrogen at 0° C. became 0·9999 litre when diluted with one-third of its volume of nitrogen, at atmospheric pressure, what effect would these deviations have on the determination? (Manchester B Sc.)

17 State the principles involved in the accurate determination of atomic and molecular weights by the measurement of gas densities, and describe in detail the necessary steps in determining the atomic weight of hydrogen with reference to oxygen by this method. Discuss the relative advantages of the gravimetric and gas density methods of determining atomic weights. (London B Sc.)

18. Discuss the significance of gas density or vapour density measurements in connexion with (*a*) the determination of atomic weights, (*b*) the occurrence of association or dissociation. How is the degree of dissociation of a partly dissociated vapour deduced from the observed vapour density? (London B.Sc.)

19. By what methods of reasoning have chemists come to the conclusion that the molecular weight of a substance is twice its vapour density? (Bristol Inter. B.Sc.)

20. Explain 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.

21. A metal forms three volatile chlorides containing 23·6, 38·2, and 48·3 per cent. of chlorine, respectively, The vapour densities of these chlorides (H = 1) are 74·6, 92·9, and 110·6 respectively. The specific heat of the metal is 0·055. Find the *exact* atomic weight of the metal and the formulae of its chlorides (O = 16·0, Cl = 35·5).
(London Inter B Com.)

22 By heating 1·2169 grams of the chloride of a metal with concentrated sulphuric acid 1·3270 grams of the sulphate were obtained. The specific heat of the metal is 0·0314 Calculate its atomic weight.
(London Inter B Sc.)

23 Describe any method used for determining the vapour density of a substance which dissociates on heating At 230° C the vapour density of phosphorus pentachloride is 4·134 (air = 1) Find the degree of dissociation. What would be the effect on the dissociation of . (i) reducing the pressure, (ii) reducing the temperature, (iii) adding nitrogen to the mixture? (Weight of 1 litre of air at S.T.P. = 1·293 grams)
(London Inter. Coll. Schol. Board.)

CHAPTER X

1. Give an account of (*a*) a method of obtaining pure oxygen in the laboratory, and (*b*) a modern industrial method of preparing oxygen from the atmosphere, explaining briefly the principles involved in (*b*). For what purposes is oxygen used? (London Inter.)

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 experiments which illustrate the combustion of substances in oxygen. Are the terms " combustible " and " supporter of combustion " entirely satisfactory?

4. 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?

5. 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?

6 What do you understand by catalysis ? Give examples and describe one chemical process in which catalysis plays an important part. (Inter B Sc. Wales.)

7 What do you understand by the statement that manganese dioxide catalyses the decomposition of potassium chlorate ? How would you find out if copper oxide also catalyses this reaction, and how would you compare its efficiency as a catalyst with that of manganese dioxide ? (London Inter. B Sc.)

CHAPTER XI

1 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 and from water gas

2 Discuss *one* of the following topics (*a*) the sorption of hydrogen by palladium, (*b*) the photochemical union of hydrogen and chlorine, (*c*) complex ions (London B Sc)

3 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 ?

4 State and explain (*a*) Avogadro's Law, (*b*) Graham's law of diffusion of gases A non-metallic gaseous oxide is found to contain 36 36% of oxygen The gas diffuses at the same rate as carbon dioxide Calculate (*a*) the equivalent weight of the non-metal, (*b*) the exact molecular weight of the gaseous oxide [C = 12, O = 16] (London Inter)

5 Give a short account of the chief methods employed for the production of hydrogen and of oxygen on a manufacturing scale, and state the chief industrial uses of these gases (London B.Sc)

CHAPTER XII

1. To what causes is the hardness of water due ? How is it estimated ? How is hard water softened (*a*) for drinking purposes, (*b*) for industrial purposes ? What is the action of hard water on soap ? (London Inter. B Com)

2 Describe the permutit process of water-softening. What are the causes of hardness in water ? What are the disadvantages of hard water ? Give an account of the various methods used for softening water (Bombay Inter B Sc.)

3. Describe experiments by which you can prove that there are at least two atoms of hydrogen in a molecule of water. (Calcutta Inter)

4 In what respects does ordinary tap water differ from water recently distilled ? What experiments could be performed to illustrate the differences you mention ? (London Inter. B.Sc.)

CHAPTER XIII

1. Discuss the views held at various times on the nature of chlorine and hydrochloric acid. (London B.Sc.)

2. Give a short account of the discovery of oxygen by Priestley, of chlorine by Scheele, and of potassium by Davy. (London Inter.)

3 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.

4 Discuss *one* of the following topics · (*a*) the sorption of hydrogen by palladium , (*b*) the photochemical union of hydrogen and chlorine , (*c*) complex ions. (London B Sc)

5 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.

6 How would you proceed to investigate the action of pure gaseous hydrochloric acid on aluminium, giving a sketch of the apparatus you would employ and a full account of the work (Bristol Inter B Sc)

7 Describe the manufacture of chlorine by the Deacon process, and give an account of the theory of the reaction. How is potassium chlorate manufactured from chlorine ? (London Inter B Sc)

8. What methods do we possess for increasing the velocity of a chemical reaction ? Illustrate each. (Bristol Inter B Sc)

9 What are the characteristics of (*a*) an acid, (*b*) a base, and (*c*) an acid salt ? Give your reasons for regarding hydrochloric acid, sulphuric acid and phosphoric acid as monobasic, dibasic and tribasic respectively, and give the method you would use for the preparation of an acid salt of one of these acids 0·75 gm of an acid of molecular weight 90 required for neutralisation 16 67 c cms of normal sodium hydroxide solution Calculate the basicity of the acid (London Inter)

10 What methods are commonly employed in the laboratory to hasten the progress of a chemical reaction ? Give examples of the use of the various methods (Joint Matric. Board Senior School Cert.)

CHAPTER XIV

1 What is meant by constant valency, varying valency, saturated and unsaturated compounds, double linkages, molecular compounds ?

2 Classify the common elements according to valency. Write down the formulae of bismuth sulphate, aluminium silicate, barium phosphate, calcium permanganate, silicon carbide, ferric phosphate.

3. Write an essay on *one* of the following (1) Atomic weight determination of elements (solids) (2) Residual and Normal Valencies. (3) Rare Gases. (Punjab University)

CHAPTER XV

1. How is the pressure of a gas accounted for on the kinetic theory ? Show how the pressure may be calculated from the molecular velocity. 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 ? (London B.Sc.)

2. 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 ?

3 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.

4 What is meant by the Avogadro number and what is its significance in chemical theory ? Describe briefly *two* methods by which this quantity may be determined (London B Sc)

5. Give an account of the kinetic theory of gases What is the experimental basis of this theory ? The relative rates of diffusion of oxygen, hydrogen and nitrogen were found to be respectively 1, 3·96 and 1·057 What deductions may be drawn from these figures concerning the density of nitrogen ? (Bombay B A)

6 The gas laws are not obeyed by nearly all gases Point out the causes which account for this behaviour and give the corrected gas equation (Bombay B A.)

7 Acetic acid is said to be " associated " (*a*) in the gaseous state, (*b*) in the liquid state, (*c*) when dissolved in certain solvents What evidence can be quoted in support of these statements ? (London B Sc)

8. Discuss the experimental evidence in favour of the real existence of molecules (London B Sc)

9. Give a brief account of the methods used for determining the molecular weights of substances in the liquid state (pure liquids), and state what classes of substance give abnormal results To what extent do the results obtained correspond with the molecular weights of the same substances in solution ? (London B.Sc.)

CHAPTER XVI

1 Write a general account of the conduction of electricity through solutions of salts (London B Sc)

2 Define the terms specific and equivalent conductivities. How is the equivalent conductivity of an electrolyte measured and how does it vary with dilution ? (Bombay B A.)

3 An electric current is passed between platinum electrodes through solutions of copper sulphate, silver nitrate and dilute sulphuric acid, the solutions being placed in series Explain what happens in each case. If 0·105 gram of copper is deposited by the current from the first solution, calculate (*a*) the weight of silver separated from the second solution, (*b*) the volume of hydrogen measured at 15° C. and 740 mm. which is liberated from the third solution (H = 1 ; Cu = 63·5, Ag = 108)
(Northern Universities Higher School Cert.)

4. Describe with experimental details the method of measuring the equivalent conductivity of a given solution. At 18° the equivalent conductivity of HI at infinite dilution is 384 ohm^{-1} and the specific conductivity of a 0·405*N* solution is 0·1332 ohm^{-1} What is the degree of dissociation and the concentration of H ions in this solution ?
(Bombay B.A.)

5. The same electric current is passed through acidulated water and through a solution of the chloride of a metal *X*. The volume of hydrogen liberated (at S T.P.) was 14·8 litres and the weight of metal deposited

42 grams. The specific heat of the metal is 0·094. Find the formula of the chloride. (London Inter. Coll. Schol. Board)

6 The electrolytic decomposition of salts in aqueous solution is frequently accompanied by secondary changes which take place at the electrodes. Give an account, with illustrations, of the character of these secondary changes Explain also the manner in which the concentration of the electrolyte is affected by electrolysis, and indicate the significance of these changes of concentration (London B Sc)

7 State the Laws of Electrolysis The same current is passed through acidulated water and a solution of stannous chloride What volume of detonating gas, measured dry at 0° C. and 760 mm pressure, is evolved from the water when 1 gram of tin is deposited from the other solution? (Sn = 119, H = 1, O = 16)

(London Inter Coll Schol Board.)

8 What is meant by the "molecular conductivity" of a dissolved electrolyte? What results have been obtained and what theoretical conclusions have followed from the measurement of molecular conductivities at different dilutions? If the molecular conductivity of sodium chloride is 110·3 mhos [ohm^{-1}] at infinite dilution and 92·5 mhos when the concentration is 0·1 mol per litre of solution, what is the degree of dissociation of the sodium chloride? (London B Sc)

9 What is Kohlrausch's Law of the independent migration of the ions? Explain the nature of the experimental data on which this law is based (London B Sc)

10. State Faraday's Laws of Electrolysis. A current is passed through two electrolytic cells in series containing, respectively, dilute sulphuric acid and a fused aluminium salt. What weight of aluminium will be obtained when 10 litres of detonating gas (at S T P) have been evolved from the dilute sulphuric acid? (H = 1, O = 16; Al = 27)

(London Inter B.Com)

11. State Faraday's Laws of Electrolysis State exactly what changes occur (i) at the electrodes and (ii) in the solution when solutions of (*a*) sodium sulphate, and (*b*) copper nitrate are electrolysed between platinum electrodes What weight of copper will be deposited on the cathode when a solution of copper sulphate is electrolysed by a current of 5·5 amperes for 1·25 hours? (Cu = 63·5, H = 1·0)

(London Inter Coll. Schol. Board)

12. Give an account of the principal phenomena of electrolysis A solution of a salt of a metal of atomic weight 112 was electrolysed for 15 minutes with a current of 1·5 amperes The weight of metal deposited was 0·783 grams. Find the valency of the metal in the salt.

(1 coulomb deposits 0·0003264 gram of bivalent copper. Atomic weight of copper = 63) (London B Com)

13. What do you understand by the terms "strong" and "weak" acid? How is the strength of an acid determined? Arrange the following acids in order of their strengths: nitric acid, trichloracetic acid, boric acid, phosphoric acid, sulphuric acid, acetic acid.

(London B.Sc.)

14. During electrolysis the concentration of electrolyte usually changes to different extents around the two electrodes. Show how this may be applied in determining the relative velocities of migration of the ions and describe an experimental arrangement used for this

purpose The ratio of the velocities of migration of the H and Cl ions is 5 to 1. A solution of hydrochloric acid is electrolysed by a current of 1 ampere for fifteen minutes Calculate the weights of HCl lost around the anode and cathode respectively (H = 1 ; Cl = 35·5 , 1 gm equivalent of an ion transports 96,500 coulombs.) (London B.Sc.)

CHAPTER XVII

1. Write a short essay on *one* of the following : (*a*) thermal dissociation, (*b*) osmotic pressure, (*c*) the colloidal state (London Inter)

2 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 ?

3 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 ?

4. 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 is 98·9 . what is the conductivity of the above solution ?

5 A solution containing 1·9 gram-molecules of calcium chloride per litre has the same osmotic pressure as a solution of cane-sugar containing 4·05 gram-molecules per litre Find the degree of ionisation of the calcium chloride. How is the osmotic pressure of a solution determined ? (London Inter. B.Sc)

6. What do you understand by a colloidal solution ? Describe the preparation of a colloidal solution of a metal How may a colloid be separated from a crystalloid with which it is in solution ? Give an illustrative example (Central Welsh Board Higher)

7. Justify the statement that a dilute solution behaves in a manner similar to that of a gas. The osmotic pressure of a solution of 0·184 gm. of urea in 100 c c. of water was 56 cm of mercury at 30° C. Calculate the molecular weight of urea given the value of R in litre atm. units = 0·082. (Bombay B.A)

8. What are colloids ? How would you proceed to prepare a colloidal solution of platinum ? How do colloidal solutions differ from ordinary solutions ? Describe the various methods by which the coagulation of a colloidal solution can be brought about. (Bombay B A.)

9. Define (*a*) isotopes of an element, (*b*) colloidal solution, (*c*) specific conductivity of an electrolyte, (*d*) equivalent weight of an element, (*e*) valency of an element. Write a short note on Hess's Law of Constant Heat Summation. (Bombay B.A.)

10. Explain how the freezing point of a solution gives information as to the molecular weight of the solute. Describe any such experiment in detail. The freezing point of a solution containing 20 grams of ammonium nitrate in 100 grams of water is −6·9° C. Calculate the molecular weight of ammonium nitrate and comment on your result. (Molecular lowering : 1·86° per 1000 grams of solvent.) (Bombay B.A.)

11. How would you prepare a colloidal solution of either silicic acid or arsenic sulphide or ferric hydroxide ? Describe the important properties of colloidal systems. (Bombay B.A.)

12 When 0·5 gram of sodium chloride was dissolved in 50 grams of water the freezing point of the water was depressed 0·617° C. The molecular depression for water is 18·5° C Calculate the apparent molecular weight of the dissolved salt and explain the result obtained What other solvents are usually employed in determining molecular weights by this method ? (London Inter B Sc)

13. What do you understand by the osmotic pressure of a substance in solution, and how is it determined experimentally ? According to Pfeffer a 4 per cent. solution of sugar showed an osmotic pressure of 2082 mm. of mercury at 15° C. Calculate the molecular weight of the sugar. (Central Welsh Board Higher)

14 What methods can be used to determine the molecular weight of a substance in solution ? Describe one method in detail and indicate as far as you can the theoretical principles which underlie it (London B Sc)

15. What are the laws governing the normal effect which a solute has on the freezing point of a solvent ? Indicate briefly the conditions which give rise to abnormal effects When 0·3 gram of a substance with molecular weight 150 is dissolved in 42 grams of a certain solvent, the freezing point of the latter is lowered by 0·233° When 0·27 gram of another substance is dissolved in 56 grams of the same solvent, the observed depression of the freezing point is 0·218°. Calculate the molecular weight of the second solute (London B Sc)

16 Define the exact meaning of the term " the osmotic pressure of a solution," and explain how it may be measured What important laws have been deduced from measurements of osmotic pressures, at different temperatures and concentrations, of different substances in solution ? (London B Sc)

17 Discuss the typical properties of colloidal solutions and give two methods for preparing such solutions. Define the terms *dialysis* and *reversible colloid*. What do you expect to see when a colloidal solution of gold is treated as follows . (*a*) a beam of light is passed through it, (*b*) an electrolyte is added ? (Bristol H S Cert)

18. Write an account of the experimental determination of molecular weights of dissolved substances by the freezing point method.

A solution of 2·02 gms of an organic acid when dissolved in 50 gms of acetic acid lowered the freezing point by 1·215° C Find the apparent molecular weight of the acid. (Molecular depression of the freezing point for acetic acid, referred to 1000 gms. =3·9°.) (London Inter. B Sc)

19. What is meant by osmotic pressure ? How have osmotic pressures been directly measured ? What are the laws of osmotic pressure ? An aqueous solution containing 1 gram of a substance in 100 c.c. had an osmotic pressure at 6·8° C. of 0·664 atm. Find the molecular weight of the substance. (2 grams of hydrogen at S.T.P. occupy 22·4 litres) (London Inter. B.Com)

20. What is Avogadro's Law ? How is it applied in the determination of atomic weights ? According to Van't Hoff " we may apply Avogadro's Law to solutions by making use of the osmotic pressure instead of the gas pressure." Explain very briefly what is meant by this statement. (London Inter. B.Sc.)

21. The freezing point molecular depression constant of water for an unionised substance is 18·6° per 100 grams of water. A solution con-

taining one gram equivalent of potassium chloride in a thousand grams of water has a freezing point of $-3{\cdot}28°$ C. Calculate the degree of ionisation of the salt in this solution. (London Inter. B.Sc.)

CHAPTER XVIII

1. 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° ?

2. Name three chemical reactions in which ozone is produced. What tests would you apply to determine whether the gas was ozone or any other oxidising substance which might be formed in any of the reactions? What is the action of ozone on . (i) concentrated sulphuric acid , (ii) sulphur dioxide , (iii) iodine ? (London Inter Coll Schol. Board.)

3. Write a brief historical account of the work done in determining the formula of ozone (London B Sc)

4. Write a short note on the diffusion of gases. The speeds of diffusion of CO_2 and of ozone were found by Soret to be as 0·29 is to 0·271 The relative density of CO_2 is 22 when H = 1 What is the relative density of ozone ? (Punjab B.A.)

5. Write an account of the preparation, properties and probable constitution of ozone. Give three characteristic tests for this substance. (Central Welsh Board Higher)

6. How would you prepare a sample of ozonised oxygen ? Draw a neat sketch of the apparatus you would use and mention the properties of the gas. When 150 c c of a sample of ozonised oxygen were treated with turpentine the volume was reduced by 36 c c. What changes, if any, would you notice when another 150 c c of the same mixture is heated until no further change is noticeable and finally cooled to the original temperature and pressure ? (Mysore First Cert.)

CHAPTER XIX

1. How can an aqueous solution of hydrogen peroxide be prepared ? What are its properties and uses, and how can the percentage of hydrogen peroxide in such a solution be estimated ? (London B.Sc.)

2. Give an account of the chemistry of *either* ozone *or* hydrogen peroxide and describe its uses How would you determine the percentage of hydrogen peroxide in a given solution ? (Bombay B.A.)

3. How would you prepare a concentrated aqueous solution of hydrogen peroxide ? What are the chief properties and uses of the compound ? Describe and explain what occurs when hydrogen peroxide is added to a mixture of lead dioxide and dilute nitric acid. (London Inter. B Sc.)

4. Describe briefly the preparation and properties of ozone and hydrogen peroxide How have the molecular weights of these substances been determined and what structural formulae are assigned to them ? (London Inter. B.Sc.)

5. What are the general properties of the peroxides ? Illustrate your answer by reference to the higher oxides of sodium, lead, hydrogen, and nitrogen. How would you estimate the percentage of lead dioxide in a mixture of litharge and lead dioxide ? (London B.Sc.)

6. Five c.c. of a solution of hydrogen peroxide liberated 0·508 gm. of iodine from a solution of potassium iodide. Describe in detail a volumetric method of obtaining such a result Express the strength of the hydrogen peroxide in terms of . (*a*) gms. of hydrogen peroxide per litre, (*b*) normality, (*c*) " volume " strength. (London Inter B.Sc.)

7. Write a short account of the preparation and properties of hydrogen peroxide. On what evidence was the formula H_2O_2 assigned to this substance ? (B Sc. Wales)

8. Give the general methods of preparation and properties of the " peroxides " of sodium, lead, hydrogen and nitrogen. Which do you consider to be the best formula for expressing the reactions of peroxide of hydrogen,

(Manchester B Sc)

9. Explain what is meant by the term acid. Why is sulphuric acid called a dibasic acid ? How would you distinguish between an acid oxide, a basic oxide, and a peroxide ? Describe and explain the tests you would apply. (Joint Matric. Board.)

CHAPTER XX

1 State the law of mass action. Illustrate its application by the consideration of (*a*) the manufacture of sulphur trioxide by the contact process, (*b*) the Deacon process, in each case giving the formula for the equilibrium constant (London B Sc.)

2. Give five examples of reversible reactions and indicate in each case the conditions under which the reactions you describe take place (London Inter B Sc)

3. Write short notes on any *four* of the following . osmotic pressure, hydrolysis, ions, reduction, passivity of metals, exothermic reactions, catalysis. (Bombay Inter B Sc)

4. Explain Ostwald's dilution law for weak electrolytes. How is it used for the determination of the relative strength of an acid ? (Bombay Inter. B.Sc.)

5. Write short notes on any *three* of the following : hydrolysis, eutectic mixtures, isotonic solutions, isomorphism (Bombay B.A.)

6. State and explain any *two* of the following (*a*) Graham's law of diffusion, (*b*) Faraday's laws of electrolysis, (*c*) Gibbs's phase rule, (*d*) Law of mass-action (Bombay B.A)

7. What is the molar concentration of a solution of sulphuric acid, 25 c c. of which gave 1·167 gms. of barium sulphate on precipitation with barium chloride ? What is the normality of the same solution ? (S = 32, Ba = 137·4). (Bristol Inter. B.Sc.)

8 What is meant by velocity of reaction ? How is velocity of reaction connected with the concentrations of the reacting substances, the numbers of molecules taking part in the reaction, and the temperature ? (London B.Sc.)

9. What is meant by Thermal Dissociation ? How may the degree of dissociation of a gas or vapour be measured ? The vapour pressure of solid NH_4HS at 25·1° C. is 50·1 cm. Find the total pressure developed at equilibrium when excess of solid NH_4HS is introduced into a vessel

at 25 1° C originally containing ammonia gas at 32 cm. pressure The vapour of NH_4HS may be taken as completely dissociated in both cases. (London B Sc)

10 Describe carefully and explain experiments you have seen illustrating (*a*) the relative strengths of acids, (*b*) dialysis, (*c*) mass-action, (*d*) the mechanism of the neutralisation of an acid by a base according to the theory of ions. (London Inter. B Sc)

11 Give a general account of the law of mass-action, and explain its application to the condition of equilibrium (*a*) in the system $NO_2 - N_2O_4$, (*b*) in the system $CaCO_3 - CaO - CO_2$

At 49·7° and under a pressure of 182 mms of mercury the density of nitrogen peroxide was 1·89 whilst that of the undissociated peroxide was 3·18 [air = 1]. Calculate the degree of dissociation and the dissociation constant At what pressure would the mixture be half dissociated ? (London B Sc)

12 Describe briefly the theory of electrolytic dissociation Explain on the basis of this theory the following experiments

(*a*) The precipitation of sodium chloride from its saturated solution by passing hydrogen chloride through the solution

(*b*) The separation of copper from cadmium in Group II. by means of potassium cyanide

(*c*) The alkaline reaction of sodium hypochlorite

(London Inter. Coll. Schol. Board.)

13 Write a short account of the views now held as to the nature of the acids and bases Suggest a method for comparing the strengths of two acids Explain why the aqueous solution of the normal salt of a strong base with a weak acid has an alkaline reaction towards litmus. (Central Welsh Board Higher)

14 Give three examples of a reversible chemical change and state what factors determine the position of equilibrium in such changes. A closed glass bulb contains ammonium bromide in equilibrium with its dissociation products What will be the effect of (*a*) raising the temperature of the bulb, (*b*) introducing hydrogen until the pressure is doubled, (*c*) half filling the bulb with glass beads Give reasons for your answers. (Madras Inter)

15. What are the conditions affecting the progress of a chemical reaction ? Give an account of any quantitative law which applies to any *one* of these conditions, and illustrate its application to any particular reaction. (London B.Sc)

16 Give a general account, with reference to the principles involved, of the effects of pressure and temperature changes on (*a*) the equilibrium between ice and water, (*b*) the dissociation of nitrogen peroxide (London B.Sc.)

17. State the principle of Le Chatelier Illustrate by examples its application in the prediction of the effects of temperature and pressure on systems in equilibrium. (London B.Sc.)

18. What is meant by hydrolysis ? Explain carefully how the properties of solutions of (*a*) potassium cyanide, (*b*) ferric chloride, (*c*) trisodium phosphate (Na_3PO_4) illustrate your answer. (London Inter. Coll. Schol. Board.)

19 What do you understand by the term " solubility-product " ? How do you explain the fact that zinc is precipitated by H_2S as a sulphide in the presence of an excess of sodium acetate, but not in the presence of strong mineral acids ? (London B.Sc.)

20. One litre of a saturated solution of barium sulphate at 25° contains 0·00233 gram of the salt Calculate the solubility product What will be the solubility of barium sulphate at 25° in 0·1M ammonium sulphate, assuming complete dissociation of the latter ? [Ba = 137, S = 32] (London B Sc)

21. Write a short essay on chemical equilibrium with special reference to (*a*) the meaning of the term, (*b*) the factors which determine the condition of equilibrium Give examples (Northern Universities Higher School Cert)

22. Distinguish between double salts and complex salts, and discuss the nature of alum, potassium silver cyanide, potassium platinichloride and sodium sulphoantimonate (B Sc Wales)

23. Explain the meaning of the following terms, illustrating your answer, where possible, by examples solubility product, thermal dissociation, electrolytic dissociation constant, partition coefficient. (London B Sc.)

24. What explanation do you offer for the following facts. A solution of sodium carbonate in water gives an alkaline reaction, whereas the bicarbonate is neutral Sodium sulphate gives a neutral aqueous solution, but one of sodium bisulphate is acid (Bristol Inter. B.Sc.)

CHAPTER XXI

1 What substances are produced when chlorine is passed to saturation into (*a*) an aqueous solution of ferrous chloride, (*b*) a cold saturated solution of potassium iodide, (*c*) a suspension of calcium carbonate in water, (*d*) ice-cold water ? (London Inter)

2 Describe and explain the behaviour of an aqueous solution of chlorine (*a*) when exposed to sunlight, (*b*) when distilled, (*c*) when added to a cold solution of sodium hydroxide, (*d*) when added to a suspension of chalk, (*e*) when added to a suspension of yellow mercuric oxide. (London Inter)

3 What is bleaching powder and how is it made ? For what purpose is bleaching powder used ? How may (*a*) a solution of hypochlorous acid, (*b*) chlorine, (*c*) oxygen be prepared from bleaching powder ? (London Inter.)

4 By what methods are the following now prepared on an industrial scale carbon disulphide, bleaching powder, aluminium ? For what purposes are they used ? What is the effect of prolonged storage on bleaching powder ? (London Inter. B Com.)

5 Given chlorine, caustic potash and concentrated sulphuric acid, how would you prepare (*a*) a solution of hypochlorous acid, (*b*) perchloric acid, (*c*) chlorine dioxide ? What is the action of chlorine dioxide on caustic potash solution ? (London B.Sc.)

6. State Hess's Law. By the solution of 10 grams of metallic sodium in much water 18,800 g. cal are liberated, and by the solution of 20 grams of sodium oxide (Na_2O) under the same conditions 20,400 g. cal.

are liberated. What is the molecular heat of formation of sodium oxide (Na_2O) if the molecular heat of formation of liquid water from gaseous oxygen and hydrogen is 68,000 g. cal ? (Bombay B.A.)

7 Define endothermic and exothermic reactions The heats of formation of CO_2, liquid H_2O, and C_2H_4 at 17° and at constant pressure are 96,960, 69,360, and −2,710 g cal. respectively What is the heat of combustion of C_2H_4 at 17° to CO_2 and liquid H_2O (*a*) at constant pressure, (*b*) at constant volume ? (Bombay B.A.)

8. You are given solid potassium chloride Starting with this compound, how would you prepare purified samples of the potassium salts of the oxy-acids of chlorine ? What is the action of (1) hydrochloric acid, and (2) concentrated sulphuric acid on each of the compounds prepared ? (Mysore Inter.)

9 When one mol of hydrogen peroxide in aqueous solution is decomposed by platinum black there is an evolution of 23·06 k cal Given that the heat of formation of one mol of liquid water is 68·36 k. cal, find the heat of formation of H_2O_2

10 The heat of combustion of carbon oxysulphide (COS) is 131·01 k. cal Given that the heats of formation of CO_2 and SO_2 are 96·96 k. cal. and 71·08 k cal., find the heat of formation of COS.

11. Explain the terms exothermal and endothermal reactions What connection exists between the thermochemical nature of a reaction and the stability of its products ? Illustrate your answer by *two* examples from each class of such reactions The heat of combustion of carbon to carbon dioxide is 96,960 g cal., and that of carbon monoxide to carbon dioxide 67,960 g cal, both at constant pressure What is the heat of formation of carbon monoxide at constant pressure ? (Joint Matric. Board Higher Cert)

12 Give three examples of reactions which are (*a*) exothermic, (*b*) endothermic. The heats of combustion of benzene, toluene and *p*-xylene are respectively 783,400, 953,900 and 1,087,700 g. cals. and the heats of formation of carbon dioxide and liquid water are respectively 94,300 and 68,400 g. cal. Calculate the heats of formation of benzene, toluene and *p*-xylene. (Bombay B.A)

13 How are chlorates and perchlorates prepared ? For what purposes are they used ? By what reactions are chlorates distinguished from perchlorates and hypochlorites ? (Punjab B A)

14. Define *heat of formation* and *heat of combustion*, and explain how a knowledge of these quantities enables heats of reaction to be calculated. The heat of combustion of carbon is 97 k cal., that of carbon monoxide is 68 k. cal. Deduce qualitatively from these data the direction in which the equilibrium $CO_2 + C \rightleftharpoons 2CO$ will be displaced on raising the temperature. (London B.Sc.)

15. Describe briefly *two* methods used on the large scale for the preparation of chlorine. How is chlorine used in the preparation of (*a*) bleaching powder, (*b*) potassium chlorate ? (London Inter. B.Sc.)

16. How are chlorine monoxide and chlorine dioxide respectively prepared ? What is the effect of heat on each, and how does each react with aqueous potash ? (Central Welsh Board Higher.)

17. State what is meant by the valency of an element and explain how it may be determined. Discuss the use of the conception of valency

to the chemist and show how the valency of an element is related to oxidation and reduction changes. Illustrate your answer as far as possible by examples. (Central Welsh Board Higher.)

18. What formulae have been suggested for bleaching powder? Give an account of the evidence upon which the accepted formula is based. (London Inter. B.Sc.)

19 Deduce the heat of formation of nitric acid in dilute solution ($H . N . O_3 . Aq$) from the following data ·

$(N . O) = -21{\cdot}6$ cal. $(2NO\ O_2) = 40{\cdot}5$ cal.
$(H_2 . O) = 68{\cdot}4$ cal. $(N_2O_4 . Aq . O) = 33{\cdot}8$ cal. (B.Sc. Wales.)

CHAPTER XXII

1. Describe the methods used for the preparation of bromine in the laboratory and in industry. How is bromic acid prepared? What are the properties of bromic acid, and its salts? How may a bromate be distinguished from a chlorate and an iodate?

2 Explain the method of extracting iodine from the mother liquors of the Chile saltpetre manufacture What action has each of the following substances upon the element nitric acid chlorine, potassium chlorate, sulphurous acid? Specify the conditions needed for the reactions given (London B Sc)

3. Describe the method used in the manufacture of bromine How is potassium bromide obtained from it on the large scale? Describe the preparation in the laboratory of (*a*) potassium bromate, (*b*) gaseous hydrogen bromide from bromine. (London Inter B Sc)

4. From what sources is iodine obtained? Describe one method by which iodine is prepared. What is the action of iodine on (*a*) sodium thiosulphate, (*b*) hydrogen sulphide, (*c*) sodium hydroxide, and (*d*) metallic mercury? (London Inter Coll. Schol. Board)

5 State briefly how the hydrogen compounds of the halogens are prepared in the laboratory Describe what takes place when (*a*) hydrogen iodide, (*b*) a mixture of equal volumes of hydrogen and iodine vapour, is heated to 444° for several hours. Mention two other reactions of similar type. (London Inter. B.Sc)

6 How is iodine obtained technically? From iodine how would you prepare: gaseous hydrogen iodide, potassium iodide, iodic acid and iodine trichloride? What is the action of water on (*a*) phosphonium iodide, (*b*) iodine trichloride? (London B Sc)

7. Describe the preparation of iodine from potassium iodide. What is the action of iodine on (*a*) hydrogen, (*b*) chlorine water, (*c*) sodium thiosulphate, (*d*) nitric acid? (London Inter. Coll. Schol. Board.)

8. Describe, with essential experimental details, the preparation from iodine of gaseous hydrogen iodide, iodine pentoxide, and potassium iodide. State and explain the reactions between (*a*) chlorine and hydrogen iodide, (*b*) sulphur dioxide and iodic acid in solution. (London B.Sc.)

9. What experiments would you perform to show that iodic and hydriodic acids react together according to the equation $HIO_3 + 5HI = 3I_2 + 3H_2O$? How would you make use of this reaction to determine the strength of a given solution of sulphuric acid? (London H.Sch.)

10. How may a pure dry sample of hydriodic acid gas be prepared? What is the action of this gas on the following—(*a*) hydrogen peroxide solution, (*b*) magnesium, (*c*) chlorine?
(London Inter Coll Schol Board)

11 How has fluorine been isolated? By what evidence was it shown that the element itself had been obtained? Summarise the main points in the chemical behaviour of fluorine which justify placing it in the halogen group. (London B Sc)

12 Why was fluorine regarded as an element and classed with the halogens before it had been isolated? How was fluorine isolated? Give a brief account of its chemical and physical properties
(London Inter)

13. Describe the methods by which bromine is obtained. How would you prepare from bromine (*a*) potassium bromide, (*b*) potassium bromate, and (*c*) a solution of hydrobromic acid? In what chemical properties do bromine and hydrobromic acid differ most from chlorine and hydrochloric acid? (London Inter)

14. Describe fully the characters by which fluorine and its compounds are distinguished from the other members of the halogen family In what forms does fluorine occur in nature and how may the element be prepared? (London Inter)

15 Say how you would prepare (*a*) bromine, (*b*) hydrogen bromide. How would you make an estimation of the solubility of bromine in water at the temperature of the laboratory? Sufficient detail is desired and the method of calculation must be shown
(Central Welsh Board Higher.)

CHAPTER XXIII

1 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.

2. 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

3 Define equivalent weight and molecular weight Explain briefly why the molecular weight of a gaseous substance is assumed to be twice its vapour density referred to hydrogen. One gram of the hydride of a metal yields on complete oxidation 1·2326 gram of metallic oxide and 0·1395 gram of water. The specific heat of the metal is 0·095. Find the equivalent weight of the metal in its hydride and oxide respectively, and determine its exact atomic weight. (London Inter.)

4. An element X forms a chloride which contains 29 34 per cent. by weight of chlorine and is isomorphous with potassium chloride. Calculate the atomic weight of X and explain carefully the theoretical principles you use in your calculation. [Cl = 35·5] What other experiments would you suggest to confirm the value of the atomic weight?
(London H.Sch.)

5. Define the term "equivalent" How would you determine the equivalent of copper? What further information would you require in order to calculate the atomic weight of copper from its equivalent? (London Inter)

6. If you were provided with a specimen of a solid element, how would you proceed in order to determine its exact atomic weight? (London B Com)

7 Explain carefully, illustrating your answer as far as possible with examples, the various considerations which are taken into account in fixing the atomic weight of an element whose chemical equivalent is known (Central Welsh Board Higher)

8 Discuss the nature of the observations which are required to establish the atomic weight and the molecular weight of an element. (Joint Matric Board Higher Cert)

9 Describe the various methods used for the determination of the atomic weights of elements. (Bombay B.A.)

CHAPTER XXIV

1. What methods have been proposed for the classification of the elements? Describe in detail the one which you consider has led to the greatest advancement of chemical knowledge (London H Sch)

2 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?

3 Describe carefully the physical and chemical properties of argon and potassium which may be employed to decide on the relative positions of these elements in the periodic table. In describing the determination of the atomic weights of these elements, pay particular attention to the accuracy attainable. (Punjab B A)

4. Discuss the statement that the elements in the first two (horizontal) groups of the periodic system exhibit more resemblance to each other than to those in the corresponding alternate groups, *e g* lithium has more resemblance to sodium that it has to potassium.

On what grounds can it be contended that fluorine is not rightly classed with the other halogen elements? (London B Sc)

5. Give a brief account of the discovery and general chemical relationships of beryllium, gallium and germanium. Explain why, apart from consideration of the periodic system, the atomic weights are twice, three times, and four times their equivalents respectively (London B.Sc.)

6. State Mendeléeff's Periodic Law and discuss the family relationship between carbon, silicon, tin and lead from this standpoint (Bristol H S Cert)

7. Point out the most evident regularities which exist as regards the chemical formulae of the compounds of the elements when the latter are arranged according to the periodic classification (Madras Inter.)

8. Explain briefly the method of classification of the elements according to the periodic law Mention briefly any chemical properties which justify the inclusion of carbon and tin in the same group of elements. (London Inter. B Com.)

9. Give a brief account of the periodic classification of the elements, explaining in greater detail, by reference to the nitrogen group, the importance of the periodic law in organising our knowledge of inorganic chemistry. (London Inter. B.Sc.)

10 Discuss the position of (*a*) beryllium, (*b*) thallium, in the periodic table. (Manchester B Sc.)

11. Give a short account of the system which is adopted to show the relations between the atomic weights and properties of the elements. Indicate the uses of such a system, and refer to any difficulties encountered in applying it. (Northern Universities Higher School Cert.)

12 Give an account of the periodic system of the elements, explaining particularly the meaning of the terms . group, period, short period, long period, atomic number, isotope. (Bombay B.A.)

CHAPTER XXV

1. " Prout's hypothesis is tempting in its simplicity, and for a time was favourably received by chemists, excepting those who had made accurate atomic weight investigations " (Lothar Meyer, 1891). Discuss this statement in the light of modern *experimental* discovery. (London B.Sc)

2. Explain how X-rays have been used to study the internal structure of crystals.

3. The " atomic weight " of fluorine is 19, but its " atomic number " is 9 Explain the distinction between the two terms. What light has modern discovery thrown on the periodic classification, especially with regard to (*a*) elements which are abnormally placed, (*b*) elements hitherto unknown. (London B.Sc.)

4. Trace the historical development of the modern idea of a chemical element. (London B.Sc.)

5. Write an essay on *one* of the following :

(*a*) The peculiarities of the colloidal state as they affect analytical chemistry

(*b*) Dissociation by heat, and the influence of traces of moisture

(*c*) Positive ray analysis (London B Sc)

6 Write short essays on *two* of the following subjects (*a*) the permutites ; (*b*) the *chemical* properties of the radio-elements ; (*c*) the technical production of hydrogen ; (*d*) isomerism in inorganic compounds ; (*e*) the position of hydrogen in the periodic table. (London B.Sc.)

7 Write an essay on the discovery of radioactivity and its effect on chemical theory. (London B.Sc)

8. How is variable valency explained in the light of the theory of atomic structure ?

9. Give a concise general account of the structure of atoms as set forth in the theory of Bohr and its later developments, and show how the arrangements of electrons assumed are capable of explaining : (*a*) the properties and existence of the rare-earth elements, (*b*) the properties of the " transitional " elements (in the wider sense). (Civil Service Comm.)

10. What types of valency are recognized in modern chemical theory? Give examples of compounds illustrating each type and write down their electronic formulae. (Civil Service Comm.)

11 Outline the chief phenomena of radioactivity, indicate the current explanation of them and show briefly how this has contributed to our ideas of atomic and molecular structure (London B Sc.)

12. How is variable valency explained in the light of the theory of atomic structure?

13 Give an account of the ammine compounds of cobalt and platinum Explain how the constitution of these compounds is usually represented, and show by diagrams that isomerism is possible. (London B Sc.)

CHAPTER XXVI

1 Define allotropy. Mention any three elements which exist in allotropic forms and give a list of all the allotropic forms of each of the elements mentioned. Indicate briefly the differences these allotropic forms show in their properties (Bombay Inter B Sc.)

2. How is sulphur obtained (*a*) from natural sources, (*b*) from alkali waste? Give a short account of the chief chemical properties of the element Briefly outline a method of preparation of pure sulphur dioxide and pure hydrogen sulphide, and show how the latter reacts with aqueous solutions of iodine, ferric chloride, zinc sulphate, potassium dichromate (Joint Matric Board Higher Cert.)

3 Give all the arguments you can which agree with the fact that oxygen and sulphur fall in the same group of the periodic table (London Inter-Coll Schol Board.)

4 Give an account of the sulphides of hydrogen Assuming that a monoxide of sulphur can exist, describe in full detail the experimental method you would suggest for the isolation of this compound (London B Sc.)

5 Discuss the application of the phase rule to the conditions of equilibrium in the cases of (*a*) sulphur, and (*b*) sodium sulphate and water. (B.Sc. Wales.)

6 Describe and explain what is observed when roll sulphur is heated in a glass flask to the boiling point What different varieties of sulphur exist, how are they prepared, and what are their properties? (London Inter B Sc.)

7. How is sulphuretted hydrogen prepared? How may it be purified? What is the nature of a solution of this gas in water and what is the action of caustic soda on this solution? What takes place when this gas is passed through acidified solutions of the following silver nitrate, arsenic chloride, ferric chloride, potassium permanganate? (Bristol Inter. B Sc.)

8 Discuss with the aid of the phase rule (*a*) the allotropy of sulphur, (*b*) the absorption of hydrogen by palladium. How can the phase rule be used to determine if yellow phosphorus and sulphur form compounds or not when they are fused together? (London B.Sc.)

9. Write an account of the allotropy of sulphur. Can you suggest any causes of allotropy? In what essential points does the allotropy of sulphur differ from that of phosphorus? (London Inter.)

CHAPTER XXVII

1 Under what conditions, and with what results, will sulphur dioxide react with (*a*) concentrated nitric acid, (*b*) lead dioxide, (*c*) hydrogen sulphide, (*d*) bromine, (*e*) manganese dioxide ? Give equations for the reactions you describe. (London B Sc)

2 Describe the " Contact Process " for the manufacture of sulphuric acid What action has sulphuric acid on (*a*) mercury, (*b*) carbon, (*c*) potassium ferrocyanide, (*d*) oxalic acid ? State in each case the conditions under which the reactions described take place (London Inter)

3 State briefly the effects on the progress and result of a reaction which may be produced by (*a*) a rise in temperature, (*b*) an increase of concentration of the reacting substances, and (*c*) the presence of a catalyst Show, by reference to not more than three cases, the importance of these effects in chemical manufacture (London Inter.)

4 Describe one method by which sulphuric acid is prepared on an industrial scale Describe the actions which may occur between sulphuric acid and (*a*) zinc, (*b*) potassium iodide (London B Sc)

5 $$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45{\cdot}2 \text{ k cal}$$

Comment on the above expression What are the conditions under which the highest technical yield of SO_3 can be obtained in this reaction ? (London Inter. B Sc)

6 Describe the behaviour of the metals copper and zinc towards (*a*) dilute hydrochloric acid, (*b*) nitric acid, (*c*) cold dilute sulphuric acid, (*d*) hot concentrated sulphuric acid (London Inter B.Sc.)

7 How are the two persulphuric acids prepared ? What formulae have been assigned to these acids, and for what reasons ? (London B.Sc)

8 Describe the preparation of sulphur chloride, sulphur trioxide, hydrogen persulphides and potassium persulphate What is the action of fairly concentrated sulphuric acid on potassium persulphate ? (London B Sc.)

9 Describe a method of preparation and the physical and chemical properties of three of the following substances a chloride of sulphur, silicon tetrafluoride, nitrogen iodide, sodium bismuthate, carbonyl chloride, iron alum, phosphonium iodide (London B Sc)

10 Give an account of the manufacture of persulphates and permanganates Describe and compare the properties of these substances Give a method for the quantitative analysis of potassium persulphate containing potassium sulphate as impurity (London B Sc)

11. How is sodium thiosulphate usually prepared ? State and explain what happens when an aqueous solution of this salt is added to (*a*) dilute sulphuric acid, (*b*) a solution of iodine in aqueous potassium iodide What use is made of this latter reaction in the laboratory ? (Central Welsh Board Higher.)

12. Write a succinct account of the chemistry of the lead chamber process for the manufacture of sulphuric acid. What is the effect of heating the following substances severally with sulphuric acid : copper, charcoal, oxalic acid ? (Central Welsh Board Higher.)

13. Give one method for the manufacture of sulphuric acid, and describe the chief properties of this substance both when hot and con-

centrated and when diluted with water Illustrate your answer with reference to its action upon (1) iron, (2) copper, (3) oxalic acid, (4) sodium nitrate, (5) calcium carbonate, (6) cane-sugar
(Aberdeen First B Sc)

14 How are sulphur monochloride, sulphur dichloride, sulphuryl chloride and thionyl chloride prepared? Describe their properties and uses (London Inter B Sc)

15 Starting with sodium sulphate and no other substance containing sodium or sulphur, state how you would proceed to obtain specimens of (i) sodium thiosulphate, (ii) caustic soda What is the action of sodium thiosulphate on (i) dilute sulphuric acid, (ii) bromine water, (iii) iodine, (iv) silver nitrate? (London Inter-Coll Schol. Board)

16 Describe the manufacture of sulphuric acid by the chamber process, laying particular stress on the functions of the Gay-Lussac and Glover towers (Bombay Inter B Sc)

17 What reactions take place between sulphuric acid and each of the following substances (i) zinc, (ii) sulphur, (iii) sodium bromide, (iv) potassium iodide, (v) potassium ferrocyanide? Indicate the most favourable conditions for the particular reactions, and where necessary point out how the nature of the reaction varies with the conditions What simple experiments would you carry out in order to demonstrate the truth of your statements? (Madras Inter)

18 When sulphur burns in air the products are sulphur dioxide and trioxide, the latter in small amount How would you burn sulphur and treat the product so as (*a*) to show that the trioxide is present, (*b*) to obtain a specimen of the dioxide free from the trioxide and from air?
(Madras Inter)

CHAPTER XXIX

1 Describe the preparation of a specimen of pure, dry nitrogen Give an account of the properties of nitrogen What differences are there between pure and atmospheric nitrogen? What other gases except oxygen and nitrogen are extracted from the atmosphere, and for what purposes are they used? (London Inter)

2 Give an account of the methods used commercially to prepare ammonia from atmospheric nitrogen Outline the evidence on which the formula NH_3 is based (London H Sch)

3. For what reasons is air considered to be a mixture and water a chemical compound? Explain in detail how you would separate in a state of purity the constituents of the following mixtures (*a*) chalk and sal-ammoniac, (*b*) sodium chloride and potassium nitrate
(London Inter-Coll Schol Board)

4 Explain fully how you would prepare pure dry ammonia and determine its density. What is the effect of (i) heat, (ii) concentrated sulphuric acid, (iii) barium hydroxide, (iv) sodium amalgam, (v) sodium hypobromite on ammonium chloride? Give equations
(Madras Inter.)

5. The formula of ammonia is written NH_3. What information does this convey to you with regard to (1) the composition of ammonia by weight, (2) the density of the gas, (3) the volume of oxygen required for the complete combustion of 1 volume of ammonia, and (4) the volume of nitrogen so obtained?

5·35 grams of ammonium chloride are heated with an excess of quicklime. What is the weight of ammonia obtained ? If it is absorbed in water to give 1 litre of solution, what is the normality of the solution ?
(Aberdeen First B Sc)

6 How would you prepare a specimen of pure ammonia gas ? Describe the properties of this substance, and state what action it has on (*a*) metallic potassium, (*b*) chlorine, (*c*) calcium chloride.
(London Inter. B Sc)

7 How would you prepare a specimen of pure nitrogen gas ? What is the action of nitrogen on (*a*) CaC_2, (*b*) Mg ? Sketch in brief outline the methods used to utilise atmospheric nitrogen
(London Inter B Sc)

8. Describe briefly the manufacture of any *two* of the following compounds (*a*) calcium cyanamide, (*b*) bleaching powder, (*c*) sodium carbonate. Explain the chemical reactions which are involved in the utilisation of the two compounds selected.
(Northern Universities Higher School Cert.)

9 What is the average composition of the air, and how can it be proved that air is a mixture, and not a chemical compound ? Describe one volumetric and one gravimetric method for determining the proportion of oxygen in the air (Aberdeen First B Sc.)

10 Discuss the effect of temperature and pressure on the equilibrium : $N_2 + 3H_2 \rightleftharpoons 2NH_3$

What other considerations besides those of equilibrium govern the industrial synthesis of ammonia ? (London B Sc)

11 What are the principal sources of the ammonium salts of commerce ? For what important purposes are the following used (*a*) ammonium chloride, (*b*) ammonium sulphate, (*c*) ammonium nitrate ? Describe carefully an experiment showing that in ammonia one volume of nitrogen is combined with three volumes of hydrogen.
(London Inter B Com.)

12 Write a short essay on " Air " (London Inter. B Sc)

13 Explain and discuss the chemical reactions involved in the chief methods employed for the fixation of atmospheric nitrogen
(London B.Sc.)

14. What methods are used in the preparation of hydroxylamine and its salts ? Discuss the reactions and constitution of this substance.
(London B Sc.)

CHAPTER XXX

1 How is nitric acid made (*a*) in the laboratory, (*b*) synthetically ? What is the effect of adding concentrated nitric acid to (*a*) antimony, (*b*) copper, (*c*) polished iron ? How does ordinary concentrated nitric acid differ in composition from fuming nitric acid ? (London Inter.)

2. How would you prepare pure nitric oxide ? How has the composition of nitric oxide been established ? (London Inter.)

3. How would you prepare (*a*) nitric acid from ammonia, (*b*) iodine pentoxide from iodine, (*c*) mercuric iodide from mercury, (*d*) ferrous nitrate from iron, (*e*) nickel carbonyl from nickel ? (London Inter.)

4. Describe in the case of *one* of the elements—nitrogen, potassium *or* zinc—how its equivalent weight has been determined, and state the evidence on which atomic and molecular weights have been assigned to this element. (B Sc Wales)

5. Find the composition of nitrous oxide from the following data: volume of gas taken 10 c c ; after addition of hydrogen 28 c c , after explosion 18 c c , after addition of oxygen 27 c c , after second explosion 15 c c (Calcutta Inter)

6 Give a full account of the methods of preparation of any two of the reduction products of nitric acid, in each case commencing the preparation from this acid.

Describe briefly what you consider to be the one most characteristic property of each of the derivatives you mention (Bristol Inter B Sc)

7 Give commercial methods for the production of (*a*) hydroxylamine hydrochloride, (*b*) sodium hypochlorite, (*c*) fuming sulphuric acid, (*d*) sodium hyposulphite ($Na_2S_2O_4$) (London B Sc)

8 Describe, with equations for all reactions, the synthesis of ammonia from its elements and its oxidation to nitric acid on the large scale. State the essential conditions for the operation of the processes described (London B Sc)

9 How would you prepare a specimen of pure nitric oxide gas ? Does nitric oxide support combustion ? Give experimental evidence of your answer What is the action of oxygen on nitric oxide in the absence and in the presence of water ? (London Inter. B.Sc)

10 A mixture of 20 c c of nitrous oxide with 20 c c of nitric oxide was exploded with 40 c c of hydrogen. After the explosion 30 c c of nitrogen remained Assuming the formula of nitrous oxide, show how to calculate from this experiment the formula of nitric oxide and describe a method by which you could confirm the result (London Inter B Com)

11. What substances may be produced by the reduction of nitric acid ? Mention the conditions under which the reactions take place in each case. (London Inter. B Sc)

12. Explain the chemistry of the reactions used to differentiate between (*a*) nitrites and nitrates, (*b*) sulphites and thiosulphates, (*c*) zinc and manganese (London Inter)

13. Describe, with experimental details, the preparation in a pure condition of ozone, chromic anhydride (CrO_3), hyponitrous acid, sodium tetrathionate, monosilane (SiH_4). Discuss briefly the structures of hyponitrous acid and the tetrathionate ion (London B Sc)

14. Describe experiments showing the oxidising action of nitric acid and show how ammonia, nitrogen and oxides of nitrogen may be prepared from nitric acid. (Madras Inter.)

15. Starting with nitric acid how might the following substances be prepared from it : a hyponitrite, hydroxylamine, and hydrazoic acid ? What evidence is there which indicates the structure of these compounds ? (Manchester B.Sc)

16. Calculate the weight of 100 litres of nitric oxide measured at 25° and 740 mm. How would you distinguish between nitric oxide and (i) nitrous oxide, (ii) a mixture of equal volumes of nitrogen and oxygen? Weight of a litre of hydrogen (N.T.P.) is 0·09 gram (N = 14 ; O = 16) (Joint Matric Board Senior School Cert.)

17 Write a brief account of the typical reactions of nitrous acid By what means would you obtain from sodium nitrite (*a*) hydroxylamine, (*b*) hyponitrous acid, (*c*) amino-sulphonic acid ? (London B.Sc.)

18 Describe briefly the processes used on the large scale for the utilisation of atmospheric nitrogen, explaining how the following substances are prepared : ammonium chloride, concentrated nitric acid, sodium nitrite. (London Inter-Coll Schol. Board.)

CHAPTER XXXI

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 ? From what sources may helium be obtained ? What use is made of this gas ?

2. In what way has it been proved that atmospheric nitrogen is not a pure substance ? How has the atomic weight of the other main constituent been determined ? What other gases are present in atmospheric nitrogen ? (London Inter B Sc)

3. Set out briefly the experimental evidence which supports the following statements (*a*) the molecule of argon is monatomic, and (*b*) *either* (i) the molecular formula of ozone is O_3, *or* (ii) certain chemical reactions take place only in presence of a trace of water (London B.Sc.)

CHAPTER XXXII

1. How may the hydrogen compounds of phosphorus be prepared ? Describe their properties and compare them with those of the corresponding nitrogen compounds (London B.Sc)

2. Give an account of the preparation and properties of meta-, pyro- and ortho-phosphoric acids Indicate with the aid of structural formulae the effect of heat on each of the sodium salts of orthophosphoric acid What tests would you apply to find out if a soluble ortho-phosphate given to you is an acid or normal salt ? (Mysore First Cert)

3. Describe briefly the properties of white and red phosphorus. How may each form be converted into the other ? Starting with phosphorus, how would you prepare (i) metaphosphoric acid, (ii) phosphorus pentachloride, (iii) sodium hyophosphite, (iv) microcosmic salt ? (London Inter-Coll Schol. Board.)

4 How is phosphorus manufactured on the large scale ? Describe the preparation from phosphorus of (*a*) phosphine, (*b*) the chlorides of phosphorus, (*c*) phosphorus pentoxide. What is the action of water on these substances ? (London Inter. B.Com.)

5. Give a short account of the element phosphorus and its more important compounds.

How is phosphorus prepared from natural sources ?

How would you set about testing for a phosphate in a soil ? (Inter. B.Sc. Wales.)

6. Justify the grouping together of nitrogen and phosphorus as members of the same family of elements. To what other element does phosphorus show the closest resemblance ? Give details in support of your statement. (London Inter.)

7. Describe the differences in the properties of yellow and red phosphorus and explain how the yellow may be converted into the red modification What takes place when phosphorus is heated (*a*) in dry air, (*b*) with nitric acid ? What is the connection between the products of the two reactions ? (Joint Matric Board School Cert)

8. Give an account of the chemistry of nitrogen and phosphorus, indicating especially the chief points in which these elements resemble and differ from each other (London B Sc)

9. Describe carefully the apparatus you would employ for the preparation of phosphoretted hydrogen Compare and contrast the properties of this substance with those of ammonia and the corresponding arsenic derivative (Bristol Inter B Sc)

10. How would you prepare specimens of phosphorus trichloride and phosphorus pentachloride ? For what purposes are these compounds used ? What justification have we for taking the formula of phosphorus pentachloride as PCl_5 ? (London Inter)

11. What methods would you adopt in order to obtain (*a*) nitrogen from nitric acid, (*b*) phosphorus from phosphoric acid, (*c*) iodine from iodic acid, (*d*) sulphur from sulphuric acid ? (London B Sc)

12 How would you prepare a specimen of ortho-phosphoric acid from (1) bone-ash, (2) phosphorus ? What is the basicity of the acid ? What products does it yield when heated (1) alone, (2) with carbon ? (Aberdeen First B Sc)

13 Give an exact account of the preparation of (*a*) phosphorous acid, (*b*) phosphoric acid. What is the action of heat on these acids ? To what types of salts do they give rise ? (London Inter)

14. How would you demonstrate the preparation and properties of phosphorus trichloride and of phosphorus pentachloride ? Suggest a method for converting the pentachloride into the trichloride (Madras Inter)

CHAPTER XXXIII

1. 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 ?

2 Write a brief account of the element arsenic, its oxides and chloride. How may arsenic hydride be distinguished from the corresponding antimony compound ? (London Inter B Sc)

3. Give full experimental details of the Marsh-Berzelius test for the detection and estimation of arsenic. What other tests for arsenic are commonly used ? (London Inter B.Sc)

4. What do you consider to be the characteristic properties of (*a*) metals, (*b*) non-metals ? Under which heading would you class arsenic ? Give reasons (Madras Inter.)

5. Given arsenic, how would you make its trioxide and trichloride ? Describe their appearance and their behaviour with water and with hydrochloric acid and show how these reactions illustrate a general law of chemistry. Contrast and explain the behaviour of the chlorides of phosphorus, arsenic and barium with water. (Madras Inter.)

CHAPTER XXXIV

1. Give a concise account of the properties of the two crystalline forms of carbon. How may graphite be obtained from amorphous carbon ?

2. 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 ?

3. What reactions are supposed to take place in the combustion of hydrocarbons ? How may a mixture of hydrogen and methane be analysed by the method of fractional combustion ?

4. Calculate from the following data the percentage composition by volume 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 , 64·2 c.c. of original mixture decreased in volume by 8·76 c c on treatment with palladium.

5 Describe *one* convenient method for preparing (*a*) methane, (*b*) ethylene, (*c*) acetylene Describe the properties of these substances so as to illustrate the differences between saturated and unsaturated hydrocarbons (London Inter.)

6. How is calcium carbide usually prepared ? Explain carefully how this substance may be used for the purpose of rendering atmospheric nitrogen into a usable form (Central Welsh Board Higher.)

7. 40 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. (Punjab B A)

8. Give an account of three different types of electric furnace and the purposes for which they are employed. (London B.Sc)

9. How are the metallic carbides made ? Which are the more important ones, and what are their uses ? (London B.Sc.)

10. Describe the preparation of the more important carbides of the metals. What are their chief uses ? How can (*a*) methane, (*b*) ammonia, (*c*) cyanides, (*d*) cyanamide, (*e*) urea, be made from them ? (Manchester B.Sc)

11. Describe fully how you would determine the composition and molecular formula of marsh gas. Sketch the apparatus you would employ for this purpose. (Calcutta Inter)

12. How is methane prepared in the laboratory ? Give an account of the experiments you would perform to demonstrate three of its important properties. (Calcutta Inter)

13. A gas contains carbon and hydrogen only. Twenty c.c. of it were exploded with excess of oxygen. After cooling, the total volume of gas had contracted by 40 c.c., and on treating the exploded gas with caustic potash there was a further contraction of 20 c.c. Show how the composition of the gas may be calculated from these results. (London Inter. B.Com.)

CHAPTER XXXV

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? How has the atomic weight of carbon been determined?

2. How is carbon suboxide prepared, and what are its properties? What structural formula is given to this substance, and why?

3. How are carbon disulphide and carbon oxysulphide prepared? What are the properties of these substances? What other sulphides of carbon have been described?

4. Describe the preparation of pure carbon monoxide How is the formula of the gas established? Describe the main chemical reactions of carbon monoxide (London B Sc.)

5 Give an account of the action of steam on red-hot carbon and show how the reaction has been adapted for industrial use Name the constituents of water-gas, and indicate briefly how you would determine their proportions in a sample of the gas (London H Sch)

6 How would you prepare specimens of carbon monoxide and carbon dioxide from oxalic acid? Explain carefully how the formula of each gas is determined (London Inter-Coll. Schol. Board)

7. When phosgene reacts with ammonia, two products are formed. State fully, giving diagrams of the apparatus, (*a*) how you would prepare the phosgene, (*b*) how you would carry out the reaction, (*c*) how you would separate and identify the two products. (London B.Sc)

8. State three methods by which carbon monoxide may be prepared. Give a general account of the properties of this gas, and state its action on (*a*) metallic nickel, (*b*) oxygen, (*c*) chlorine, and (*d*) an ammoniacal solution of cuprous chloride. (London Inter-Coll Schol Board.)

9 Give a general account of the structure and luminosity of flames and of the chemical reactions occurring in them (London B Sc)

10. Describe carefully experiments you have actually seen, illustrating any *two* of the following: (*a*) the composition of steam by volume, (*b*) the law of mass-action, (*c*) the relative strengths of acids, (*d*) the structure of the Bunsen flame, (*e*) the volumetric composition of ammonia. (London Inter. B Sc.)

11. Describe the preparation and properties of the per-acids (or their salts) of sulphur, carbon and phosphorus. What structures are assigned to these compounds? (London B.Sc)

12. Explain the structure of the flames produced (*a*) by hydrogen burning in air, and (*b*) by coal gas when burnt with a variable air supply as in a Bunsen burner. Describe experiments in support of your statements. (London Inter.)

13. What is meant by the terms "combustion" and "oxidation"? Describe experiments to show the difference between the above two phenomena. (Calcutta Inter.)

14. Explain with diagrams the structure of a candle flame, and describe experiments that you have seen in support of your explanation. What is the difference between an ordinary candle flame and the Bunsen flame? (Calcutta Inter.)

15 How would you determine the composition by weight of carbon dioxide? What precautions would you take to secure accurate results? Sketch the apparatus used for the purpose. (Calcutta Inter)

16 Describe the preparation of carbon disulphide. Compare and contrast its properties with those of carbon dioxide. How would you show that one is an endothermic and the other an exothermic compound? (Central Welsh Board Higher)

17. A slow current of air is passed through a long tube packed with charcoal and heated to redness Explain in detail how you would determine the composition of the issuing gas. (Central Welsh Board Higher.)

18 How may carbon monoxide be prepared, and how may the presence of a small amount of this gas in air be detected? State how and under what conditions the gas reacts with (*a*) nickel, (*b*) chlorine, (*c*) sodium hydroxide. (London B Sc)

19. Write a short essay on *one* of the following subjects
(*a*) The relation of the electron theory to chemical action
(*b*) The passive state of metals
(*c*) The effect of traces of moisture in promoting chemical change.
(London B Sc.)

20 For what purposes are the cyanides of sodium and potassium used in industry? Describe a process used in the manufacture of *one* of them. By what reactions would you obtain (*a*) potassium cyanate, (*b*) hydrocyanic acid, (*c*) cyanogen, from potassium cyanide and ordinary reagents? (London B Sc.)

21. Describe methods of preparing (1) sodium cyanide, (2) anhydrous hydrocyanic acid, (3) a dilute solution of hydrocyanic acid, (4) cyanogen Give a brief description of the properties of cyanogen and hydrocyanic acid. (Aberdeen First B Sc)

22. What do you understand by the term *explosion*? Describe experiments in which (*a*) explosion, (*b*) quiet combustion, may be obtained with (i) hydrogen and air, (ii) hydrogen and chlorine, (iii) gunpowder. (Joint Matric. Board Senior School Cert.)

CHAPTER XXXVI

1. Mention the principal mineral sources of boron Describe how (*a*) boron, (*b*) boric acid, (*c*) borax, (*d*) potassium borofluoride (KBF_4), can be prepared from any one of these minerals. (London B.Sc.)

2. Discuss *either* (*a*) the chemical properties of magnesium in relation to those of calcium and aluminium, *or* (*b*) the chemical properties of boron in relation to those of carbon and aluminium. (London B.Sc.)

3. 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 weights of sodium and oxygen to be 22·83 and 15·88 respectively, find the atomic weight of boron.

4. 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.

5. Describe the general properties of colloidal solutions. How may colloidal solutions of ferric hydroxide and silicic acid be prepared? (London B.Sc.)

6. 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 ?

7. Starting with a reasonably pure specimen of natural silica, such as white sand, how would you prepare specimens of pure silica, silicon tetrachloride, hydrofluosilicic acid, colloidal silica, and silicon ? Indicate briefly the analogies and differences exhibited by carbon and silicon. (London B Sc)

8. How are boron and silicon prepared from their oxides ? Describe the preparation of (*a*) boron trichloride, (*b*) hydrofluosilicic acid, (*c*) boric acid from borax. (London Inter B.Com)

9 How is boron prepared in the pure condition ? Compare the properties of boron and its compounds with those of aluminium and its compounds (Bombay B.A.)

10. Describe the methods of preparation and the properties of such compounds of silicon as have a close physical or chemical resemblance to the corresponding compounds of carbon Point out, in each case, the resemblances in question. (London Inter B Sc Hons)

11 What do you know about the occurrence in nature of silica in the free and combined states ? How could you prepare a specimen of pure silica from glass, and determine the percentage of silica in a sample of water glass ? (London Inter B.Sc)

12. Describe fully the physical and chemical properties of silica. State if it is acidic or basic. In what forms does silica occur in nature ? (Allahabad Inter)

13 How is boric acid recognised in analysis ? How and why is it removed from solutions containing it which are to be tested for metals in group separation ?

14 Describe the preparation of pure boric acid from borax. How are the following prepared from boric acid · (*a*) boron, (*b*) boron chloride ? (London Inter-Coll Schol Board)

15 How are boric acid and boron prepared from borax ? Describe the properties of these substances What is the action on litmus of a solution of borax ? Explain the last result and give two other examples in which similar results are obtained (London B Com)

16. Describe briefly the chemical characteristics of boron and its compounds. Discuss the relationship of this element to (*a*) aluminium, (*b*) silicon (London B.Sc.)

17. Say briefly how the following are prepared from ordinary white sand : (*a*) silicon, (*b*) soluble silicic acid, (*c*) silicon chloride. Describe the principal properties of any *one* of them (Central Welsh Board Higher.)

CHAPTER XXXVIII

1. Describe, with examples, the general principles underlying the extraction of metals from their ores. (London B.Sc.)

2. What are the main features that distinguish metals from non-metals ? Discuss the methods of preparation and principal properties of metallic oxides. (Bristol H.S. Cert.)

3. Explain four of the following terms and give examples of their use: thermal dissociation, acid chloride, molecular constant for the elevation of boiling-point, additive compound, eutectic, the alums, ionisation. (London H Sch)

4. Classify the common metals according to their behaviour with (*a*) air, (*b*) water, (*c*) acids (London Inter-Coll Schol. Board.)

5. Describe the phenomena of the eutectic crystallisation of a binary system What would be the general character of the freezing point curve for mixtures of two metals which enter into chemical combination? Which mixtures of the two metals would solidify completely at one temperature? (London B.Sc.)

CHAPTER XXXIX

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?

2. Give an account of the main contributions to chemistry made by (*a*) Pasteur, (*b*) Dumas, (*c*) Black, (*d*) Scheele. (London B Sc.)

3. Give an historical account of the experiments which led to the isolation of (*a*) the halogens, and (*b*) the metals sodium and potassium (London B Sc.)

4. Describe an electrolytic method for the preparation of metallic sodium. What action have (*a*) ammonia, (*b*) oxygen, (*c*) chlorine, on metallic sodium? Describe the conditions under which each reaction takes place. (London Inter)

5. Explain the origin of the names "carbonate of soda" and "bicarbonate of soda." How are these compounds now designated? How is bicarbonate of soda manufactured? What would be the composition of the crystals which would separate if a quantity of "bicarbonate of soda" were dissolved in water and the solution boiled until on cooling to the ordinary temperature crystals were deposited? (London Inter)

6. Adduce evidence to show that an aqueous solution of ammonia contains the compound NH_4OH Compare and contrast the behaviour of aqueous solutions of ammonia and caustic soda respectively with solutions of (*a*) copper sulphate, (*b*) zinc sulphate, (*c*) bromine. (Central Welsh Board Higher.)

7. Explain fully, giving examples, the uses of ammonium chloride and ammonium sulphide in qualitative analysis (Central Welsh Board Higher)

8. Comment upon any *three* of the following:

(*a*) The inclusion of gold, silver and copper in the same group of the periodic classification.

(*b*) The failure of a solution of sodium hydroxide to produce a precipitate when added to a solution of copper sulphate containing glycerine.

(*c*) The acceptance of potassium as a radioactive element.

(*d*) The dark lines in the solar spectrum

(*e*) The alkalinity produced on diluting a concentrated solution of borax which had been rendered neutral to litmus.

(*f*) The fact that magnesium hydroxide is soluble in a solution of ammonium chloride, but not in either potassium chloride or sodium chloride solution. (London B.Sc.)

9. Write a short essay on *one* of the following :
(*a*) The discovery of chlorine and of its elementary nature.
(*b*) Scheele's and Priestley's work on oxygen.
(*c*) Black's work on the alkalies. (London Inter. B Sc)

10. Give an account of the manufacture from common salt of (*a*) hydrochloric acid, (*b*) washing soda, (*c*) sodium bicarbonate, (*d*) caustic soda. How would you estimate the amounts of sodium hydroxide and sodium carbonate in a specimen of commercial caustic soda ?
(London Inter. B Com)

11. Give an outline of the technical production of washing soda by *either* (*a*) the Leblanc, *or* (*b*) the Solvay process, and discuss as fully as you can the theoretical principles involved. (London B Sc)

12. Describe the manufacture from common salt of (*a*) sodium carbonate by the ammonia-soda process, and (*b*) caustic soda by an electrolytic process. What impurities are likely to be contained in commercial sodium carbonate and caustic soda, and how would you test for their presence ? (London B Com)

13 Compare and contrast the action of water on the following metals sodium, potassium, calcium, magnesium, and iron What volume of hydrogen, measured over water, at 3° and 690 mm is obtained by the action of water upon 0·91 gram of sodium ?
(Vapour tension of water at 3°, 6 mm. Atomic weight of sodium, 23)
(Aberdeen First B Sc)

14 Give a concise account of the Leblanc process for the manufacture of sodium carbonate. Indicate briefly how sodium carbonate may be converted into (*a*) sodium bicarbonate and (*b*) sodium hydroxide.
(London Inter-Coll. Schol. Board)

CHAPTER XL

1. What are the natural sources of the metals silver, nickel, mercury, chromium and lead ? Give a brief account, for two of these metals, of (*a*) the processes used in their extraction, and (*b*) the general chemistry of the metals and their relationship in the Periodic Classification
(London B Sc.)

2. Copper, silver and sodium are included in the same vertical column of the Periodic System Justify this classification by a survey of the properties of the three elements and of their principal compounds Mention any exceptions to the general similarity shown by these elements. (Bristol H.S. Cert.)

3. Give an account of either (*a*) the metallurgy of copper, or (*b*) the industrial utilisation of common salt. (London B Sc)

4. What is the action of hydrochloric acid, of sulphuric acid and of nitric acid on copper under different conditions ? State how cuprous oxide and cuprous chloride are prepared. (Bombay Inter. B.Sc)

5. How is gold extracted from its ores ? Discuss the chemical reactions involved in the methods employed. How would you prepare a pure sample of gold from an alloy of copper and gold ? (Bombay B A)

6. Name the chief ores of copper, and describe briefly how the metal may be isolated from them. Describe fully the method employed for the purification of the metal. (London Inter.)

7. Explain the chemistry of the extraction of copper from its sulphide Describe and explain the preparation of the following compounds of copper. (*a*) cupric chloride, (*b*) cuprous oxide, (*c*) cuprous chloride How does (*b*) react with the dilute mineral acids ?
(Central Welsh Board Higher)

8. Copper and silver occur in the same group in the periodic table. What objections are there to this arrangement ? Show in what respects these elements and their compounds resemble one another and how they differ (Madras Inter)

9 How may crude copper be refined ? State the physical and chemical properties of copper Write an equation showing the action of hot concentrated sulphuric acid on copper Name the elements present in two alloys of copper and state the uses of those alloys.
(Madras Inter)

10 Describe the preparation of sodium thiosulphate What are the silver salts used commonly in photography, and what are the chemical processes involved in the production of a photograph ? (Bombay B.A)

11. Name the principal ores of copper. Describe *any one* process of extracting copper from its ores Give equations. (Calcutta Inter)

12. How would you distinguish cuprous from cupric and ferrous from ferric salts ? How would you obtain ferric from ferrous sulphate and cupric chloride from cuprous chloride ? Give equations
(Calcutta Inter)

13 Zinc, copper, and iron are heated separately in a current of chlorine Describe two chemical and two physical properties of each of the compounds formed, and give their formulae. (Calcutta Inter)

14 What do you understand by the equivalent weight of an element ? Describe an experiment by which you would determine the equivalent weight of copper. (Calcutta Inter.)

15. What principles are involved in the Pattinson process for the desilvering of lead ? How would you obtain a pure specimen of silver nitrate from a silver coin ?

What reactions take place when a solution of silver nitrate is added to (*a*) a solution of sodium thiosulphate, (*b*) sodium hydroxide solution, (*c*) a solution of sodium phosphate ?
(Northern Universities Higher School Cert.)

CHAPTER XLI

1 Discuss the analogies between magnesium and calcium, strontium, and barium on the one hand, and zinc, cadmium, and mercury on the other. (London B Sc.)

2. Discuss the physical and chemical properties of the metals of the alkaline earths and their compounds, from the point of view of their inclusion in the same group of the periodic system.
(London Inter. B.Sc.)

3. What are the principal compounds of calcium occurring in nature, and how is the metal calcium prepared ? Show how (*a*) bleaching powder, plaster of Paris, and calcium cyanamide, *or* (*b*) glass, cement and mortar are prepared and used in industry. (Bombay B.A.)

4. Enumerate the most striking points of resemblance and difference among the oxides, hydroxides and salts of calcium, barium and strontium (Central Welsh Board Higher.)

5. Describe the commercial production of calcium carbide, and mention three important substances which can be technically prepared from it as a starting-point. Indicate briefly the steps in the manufacture of these substances (London B Sc.)

6 Write a short account of the alkaline earth metals (calcium, strontium, barium) and their compounds

Starting with the sulphate, describe the preparation of (*a*) one of the metals, (*b*) one of the peroxides, (*c*) a soluble salt of one of the metals. (London B.Sc.)

CHAPTER XLII

1 Describe *two* methods which may be adopted for the preparation of each of the following substances calcium oxide, boron trichloride, anhydrous magnesium chloride, silicon tetrafluoride What, if any, is the action of water on these compounds, and what are the properties of the products ? (Joint Matric Board Higher)

2. Starting with the mineral dolomite ($CaCO_3,MgCO_3$), how would you prepare, in a state of purity, samples of (*a*) magnesium sulphate, (*b*) calcium carbonate ? Full details are required (Central Welsh Board Higher)

3. Name the important ores of zinc. How is the metal extracted and purified ? State its properties and uses. (Calcutta Inter.)

4. How is zinc obtained from its ores ? From zinc how would you prepare specimens of anhydrous zinc chloride, crystallised zinc sulphate, and zinc pyrophosphate ? (London Inter.)

5. What is brass ? How is it made ? How could you prepare specimens of pure copper and zinc from brass ? Name any other well-known alloys, giving their general properties and uses. (Madras Inter)

6 Give a general account of the mercurous and mercuric salts How is Nessler's reagent made and used ? (London Inter B.Sc)

7. What are the principal reasons for placing magnesium, zinc and cadmium in the same group of the periodic table ? What principles are involved in the manufacture of metallic zinc ? Why cannot magnesium be prepared in a similar manner ? (London B Sc)

8. Describe, with essential experimental details, the preparation in as pure a state as possible of specimens of *four* of the following : cuprous sulphate, zinc chloride ; silver from commercial silver, metallic beryllium ; hydroxylamine from sodium nitrite ; sodium sulphide ; carbonyl sulphide ; nitrosyl chloride. (London B.Sc.)

9. How does mercury occur in nature and how is it obtained from its ores ? How would you prepare chemically pure mercury from a commercial specimen ? (London Inter.)

10. How is mercury obtained from the native sulphide ? Describe the preparation of the chlorides of mercury. How can these salts be distinguished from one another and from the chloride of silver ? (Aberdeen First B.Sc.)

11. Give an account of the extraction of mercury from its chief ore. How may the following be prepared from mercury; mercurous nitrate; mercuric nitrate; mercurous chloride; mercuric chloride? What is the action of heat on these substances? (London B.Com.)

12. What do you know about the vapour densities of (*a*) sulphur, (*b*) mercurous chloride, (*c*) phosphoric oxide?

The density of nitrogen peroxide at 97·5° is 25·7 (H = 1); calculate the percentage of dissociation at this temperature. (London B Sc.)

13. Describe what you see and explain the actions which take place when an aqueous solution of potassium iodide is added to aqueous solutions of each of the following: (*a*) Mercuric chloride, (*b*) lead acetate, (*c*) copper sulphate; (*d*) hypochlorous acid; (*e*) chromic acid. (London Inter B.Sc.)

14. Compare and contrast the properties of zinc, cadmium, and mercury, and of their oxides, chlorides and sulphates What are the general principles on which the production of zinc from its ores is based? (London B Sc.)

15. Under what conditions does ammonia react with the following substances: (*a*) potassium, (*b*) mercuric oxide, (*c*) mercuric chloride, (*d*) copper sulphate? Give an account of the reactions which take place and of the substances produced (Manchester B Sc.)

16. How is mercury obtained from its ores? What are the characteristic uses of the metal and on what do they depend? Describe the preparation and properties of the oxides and halides of mercury. (Bombay B A.)

17. Write notes on (*a*) partition coefficient, (*b*) constant boiling mixtures, (*c*) electrolytic solution tension of a metal, (*d*) solubility product. (Bombay B.A.)

CHAPTER XLIV

1. From what ore is the metal aluminium usually isolated, and how is the process carried out? Mention the chief properties and applications of the metal. What experiments would you perform in order to illustrate the great affinity of aluminium for oxygen? (London Inter.)

2. What do you understand by the following terms. (*a*) weak electrolyte, (*b*) amphoteric oxide, (*c*) basic salt, (*d*) freezing-point constant of a solvent? Give illustrative examples. (London Inter. B Sc.)

3. Describe the production of aluminium from bauxite. How would you obtain specimens of anhydrous aluminium chloride, aluminium oxide, and potash alum from metallic aluminium? (London Inter. B.Sc.)

4. How is aluminium obtained on the industrial scale? Describe the preparation in the laboratory from metallic aluminium of (*a*) anhydrous aluminium chloride, (*b*) alumina, (*c*) aluminium sulphate. For what purposes are these substances used in industry? (Civil Service Comm.)

5. What reasons are there for assigning the formulae NH_3 and Al_2O_3 to ammonia and aluminium oxide respectively? (H = 1; N = 14; O = 16; Al = 27.) (London B.Com.)

6. Describe and explain what happens when a solution of (*a*) sodium hydroxide, (*b*) ammonia, (*c*) sodium carbonate, is added to a solution of (*a*) aluminium chloride, (*b*) zinc chloride.
(London Inter. B Sc.)

7 Discuss the application of electrolysis to the production of the following substances. (*a*) sodium hydroxide, (*b*) aluminium, (*c*) sodium, (*d*) ammonium persulphate. (London B Sc)

8. Discuss either (*a*) the properties of thallium in relation to those of silver and lead, or (*b*) the variations of chemical character with valency exhibited by chromium and manganese. (London B Sc)

9. What do you understand by the term "amphoteric oxide"? Give two examples of amphoteric oxides, and show what action the substances you choose have with an acid and with a caustic alkali.
(London Inter-Coll. Schol. Board.)

10. Write a short account of the elements of the rare-earth group. By what methods may they be separated from one another?
(London B.Sc.)

11. State briefly how the following substances are prepared: (*a*) arsenious chloride, (*b*) boron nitride, (*c*) silicochloroform, (*d*) aluminium carbide. What chemical changes take place when they are treated with water? (London B Sc.)

CHAPTER XLV

1 What is the chief ore of tin, and how is the metal extracted from it? Describe the chief uses of the metal, its alloys and compounds. State what occurs when tin is (1) attacked by nitric acid, (2) attacked by hydrochloric acid, (3) heated in chlorine, (4) heated in hydrogen chloride, (5) exposed for a long time to a very low temperature.
(Aberdeen First B Sc.)

2. Compare the properties of the compounds of lead with those of barium, and explain why, in the periodic table, lead is not grouped with barium. (Allahabad Inter)

3. How is tin prepared from its ores and purified sufficiently for commercial purposes? How would you prepare specimens of (*a*) stannous chloride, (*b*) stannic chloride, (*c*) sodium stannate, from metallic tin? (London Inter.)

4. How do you account for the following facts:

(*a*) The solubility of lead sulphate in a solution of ammonium acetate

(*b*) The solubility of cupric hydroxide in solutions of ammonia and of potassium cyanide.

(*c*) The action of ammonium sulphide on neutral solutions of aluminium and zinc salts.

(*d*) The action of sodium acetate in allowing the precipitation of cobalt sulphide from an acid solution of a cobalt salt by hydrogen sulphide.
(London B.Sc.)

5. Describe in detail a method of extracting lead from its ores and the subsequent refining of the metal. Give an account of the working up of any impurities into commercially important products. (London B.Sc.)

6. Give an account (1) of the extraction of tin from its chief ore, (2) of the preparation and properties of the chlorides of this metal. Assign tin to its appropriate place in the periodic classification, giving reasons for your allocation. (London B.Sc.)

7 How is lead obtained from its ore galena ? How are the following compounds prepared from lead : litharge, lead dioxide, lead nitrate, lead iodide ? (London Inter. B Sc)

8. Describe the method of preparation of the three oxides of lead. What are their formulae, and how may they be distinguished ? (London Inter-Coll Schol Board.)

9 What is the effect of strongly heating in air (*a*) magnesium, (*b*) chalk, (*c*) barium peroxide, (*d*) sodium nitrate, (*e*) lead dioxide ? Describe the reactions which take place when these substances and the solid products of calcination respectively are treated with hydrochloric acid. (London Inter)

10. How is metallic tin obtained from its ores ? What are the industrial uses of tin ? Describe the preparation from tin of tin dioxide, crystalline stannous chloride, and anhydrous stannic chloride (London Inter B Com)

11. Give an account of the chemistry of *either* (*a*) tin, or (*b*) nickel. Show how the element selected is related to the other members of its group in the periodic system (London B.Sc)

12. Discuss Group IV of the periodic system, with particular reference to the acidic and basic nature of the oxides of its members (London B Sc)

13. Show that the elements of Group IV of the Periodic System (the carbon family) become increasingly metallic with rising atomic weight (London H Sch)

CHAPTER XLVI

1 Give a general account of the chemical properties of (*a*) copper, silver and gold , (*b*) thallium , (*c*) bismuth (London B.Sc)

2. Write a concise comparative account of the properties of the chlorides of the nitrogen group of elements (N, P, As, Sb, Bi) Describe how you would prepare *one* of them in a reasonably pure condition. (London B.Sc)

3 What do you know of the production and properties of the hydrides of the metals ? (London B Sc)

4. Describe the chemical properties of the elements of the nitrogen group in the periodic system In what ways are metals and non-metals usually differentiated ? Illustrate your answer by reference to the elements of the group described. (London B Sc.)

CHAPTER XLVII

1. 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 ?

2. Describe, with experimental details, the preparation in a pure condition of : ozone, chromic anhydride (CrO_3), hyponitrous acid, sodium tetrathionate, monosilane (SiH_4). Discuss briefly the structures of hyponitrous acid and the tetrathionate ion. (London B.Sc.)

3 Give an account of the reactions which take place between the following pairs of substances, and mention in each case the conditions under which the reactions occur · (*a*) potassium chromate and sulphuric acid, (*b*) nitric acid and ferrous sulphate, (*c*) iodine and sulphur dioxide, (*d*) hydrogen peroxide and chromic acid (London Inter B.Sc)

4. What is the chief ore of chromium ? Explain how, starting with this ore as raw material, you would obtain (*a*) potassium chromate, (*b*) chromium trioxide, (*c*) chromic anhydride, (*d*) chromium For what purposes is chromium mainly employed ? (London Inter)

5. Describe the preparation of sodium dichromate from chrome-ironstone (chromite) How can potassium dichromate be prepared from the sodium compound ? From potassium dichromate how would you prepare (i) chromous acetate, (ii) chromium trioxide, (iii) chromyl chloride ? Describe briefly the properties of these three substances. (London Inter-Coll Schol Board)

6 How can you prepare potassium dichromate ? What is its action on (*a*) H_2S, (*b*) SO_2, (*c*) ferrous salts ? (London Inter-Coll Schol Board)

7 Write an essay on higher oxides, with special reference to their chemical properties and constitution (London B Sc)

8 In the periodic system sulphur and chromium occur in the same group Justify this by considering the chemical properties of the two elements (London Inter-Coll Schol Board)

9 Starting with chrome ironstone, how would you prepare (*a*) potassium dichromate, (*b*) chrome alum, (*c*) chromium metal, (*d*) chromium trioxide ? (Bombay B.A)

CHAPTER XLVIII

1. Describe, with all *essential* practical details, how you would obtain specimens of · (*a*) barium chloride from heavy spar (barytes), (*b*) anhydrous magnesium chloride from carnallite, (*c*) pure silver nitrate from an alloy of silver and copper, (*d*) pure manganous chloride from pyrolusite. (London Inter. B Sc)

2 0·2015 gm. of impure manganese dioxide were heated with hydrochloric acid and the chlorine evolved was passed into a solution of potassium iodide. The iodine thus liberated required 20·5 c c $N/10$ sodium thiosulphate solution. What is the percentage of pure manganese dioxide in the sample ? Give a full account of all practical details and the precautions necessary to ensure an accurate result (O = 16; Cl = 35·5, Mn = 55, I = 127) (London Inter. B.Sc.)

3 How would you prepare in the laboratory a specimen of potassium permanganate ? A quantity of potassium permanganate was boiled with hydrochloric acid and the gas evolved was led into a solution of potassium iodide. When the reaction was complete the iodine liberated was titrated with a solution of sodium thiosulphate containing 124 grms. $Na_2S_2O_3 \cdot 5H_2O$ per litre It was found that exactly 60 c c were required to decolorise the solution of iodine. What weight of potassium permanganate was used ? (K = 39, Na = 23, Mn = 55, H = 1, O = 16, Cl = 35·5, I = 127, S = 32.) (London Inter.)

4. How is potassium permanganate prepared ? Describe the appearance of this salt and mention its chief uses (*a*) industrially, (*b*) in volumetric analysis. In the latter case give equations to show what reactions it undergoes. (Madras Inter.)

5. Describe the preparation of potassium permanganate. How would you estimate the percentage of available oxygen in a crude specimen of potassium permanganate? (Central Welsh Board Higher.)

6. How is potassium permanganate prepared? What action has potassium permanganate, in the presence of dilute sulphuric acid, on (*a*) ferrous sulphate, (*b*) oxalic acid, (*c*) potassium nitrite, (*d*) sodium sulphite, and (*e*) hydrogen peroxide?

(London Inter-Coll. Schol. Board.)

7. Describe, with essential experimental details, the preparation of (*a*) barium chloride from heavy-spar, (*b*) pure manganous chloride from pyrolusite, (*c*) concentrated hydrogen peroxide from barium peroxide.

(London Inter-Coll. Schol. Board.)

8 Give an account of the preparation, properties and probable constitution of four salts in which the acidic radical contains a metal in a higher state of oxidation (Salts containing four different metals in the acidic radicals must be described.) (Civil Service Comm.)

9. Explain fully what is meant by a decinormal solution of an oxidising agent.

Calculate the weight of potassium permanganate contained in one litre of a solution of this substance which is 1·1 $N/5$. What volume of this solution of potassium permanganate would be required for the oxidation of the oxalic acid in 25 c c of a decinormal solution of oxalic acid in presence of sulphuric acid? (H = 1, C = 12; O = 16, K = 39; Mn = 55)

(London B Com)

10. Show how the following are prepared from pyrolusite. (*a*) manganese, (*b*) potassium manganate, (*c*) potassium permanganate, (*d*) pure manganese dioxide (Bombay B.A)

11. Define fully the term oxidising agent Describe the methods and the reagents you would employ to oxidise the following substances. copper, ferrous chloride, arsenious oxide, silver, oxalic acid, lead sulphide, ammonia (London H. Sch)

CHAPTER XLIX

1. Describe the methods by which the following substances may be prepared: potassium iodide, potassium chlorate, potassium permanganate, potassium ferrocyanide.

(Northern Universities Higher School Cert.)

2. Describe how you would prepare crystallised specimens of (*a*) ferrous sulphate, (*b*) ferrous ammonium sulphate, (*c*) iron ammonium alum from metallic iron. What takes place when these substances are heated strongly? (Joint Matric. Board Higher Cert.)

3. Describe the manufacture of iron in the various forms in which it is ordinarily used. Mention briefly the properties of each form.

(Joint Matric. Board Higher Cert)

4. Discuss the reactions which take place in the blast furnace during the manufacture of iron. State what you know of the preparation and properties of the following compounds of iron: ferrous ammonium sulphate, colloidal ferric hydroxide, ferroso-ferric oxide, ferric sulphate, potassium ferrocyanide. (Joint Matric. Board Higher Cert.)

5. Give an account of the metallurgical processes involved in the manufacture of steel from pig-iron. What proportion of carbon is

necessary in mild steel and hard steel, respectively, and what views are now held as to the condition in which carbon exists in steel ?
(Punjab B.A.)

6. State exactly what you would observe on heating each of the following substances in a crucible in contact with the air : (*a*) lead, (*b*) lead dioxide, (*c*) copper, (*d*) copper nitrate, (*e*) potassium nitrate, (*f*) silver, (*g*) ferrous sulphate ($FeSO_4$, $7H_2O$) (Joint Matric. Board.)

7. State what changes occur when (*a*) potassium iodide is added to a solution of copper sulphate, (*b*) concentrated sulphuric acid is heated with potassium dichromate, (*c*) dilute nitric acid is poured on copper, (*d*) potassium permanganate is heated, (*e*) chlorine is passed over heated iron. Represent these changes by equations (London Inter. B.Sc.)

8. Which of the metals do you consider are most closely related to iron ? Give your reasons Describe a process for converting " pig " iron into steel, and explain the nature of the chemical changes involved.
(London B.Sc.)

9 Discuss any *one* of the following :
(*a*) The manufacture of steel by the open hearth acid and basic processes , *or*
(*b*) The extraction of silver from lead by the Parkes and the Pattinson processes ; *or*
(*c*) The manufacture of iron in the blast furnace. (London B.Sc.)

10 What are the chief impurities in " cast-iron " ? How would you test a sample of " cast-iron " for them ? Briefly describe the methods employed for the quantitative examination of *ordinary* steel.
(London B Sc)

11 Give an account of the reactions which take place between the following pairs of substances, stating in each case the conditions under which the reactions occur : (*a*) stannous chloride and mercuric chloride, (*b*) arsenic trioxide and nitric acid, (*c*) sand and coke, (*d*) ferrous sulphate and potassium cyanide. (London H. Sch)

12. Give an account of the commoner double and complex cyanides, indicating briefly the practical applications of their properties.
(London B Sc.)

13. What are the important ores of iron ? Discuss the chemical reactions occurring in the blast furnace Describe briefly the subsequent conversion of cast-iron into wrought iron and steel.
(London Inter. B Sc.)

14. Write short notes on *four* of the following subjects : the law of mass-action, allotropy, atomic heats, vapour pressure, the rusting of iron, catalysis. (London Inter. B.Sc)

15. A mineral consists of oxides of iron and manganese. Describe how you would prepare from it pure specimens of (*a*) iron alum, (*b*) manganese dioxide, (*c*) potassium permanganate. (London H. Sch.)

CHAPTERS L–LI

1. Give a general account of either (*a*) the common metals of Group VIII of the Periodic Table, or (*b*) the acid-forming oxides of metals and the salts derived from them. (London B.Sc.)

2. Discuss the relations of the following metals: chromium, manganese, iron, cobalt, nickel, copper, with special reference to the following points, (*a*) reduction of their oxides to the metal, (*b*) physical properties of the metals. (London B Sc.)

3. Describe the preparation and properties of one liquid compound of (*a*) chromium, (*b*) nickel, and (*c*) silicon. (London B.Sc)

4. Describe how you would prepare *three* of the following substances, and comment on any features of interest which the processes present. (1) chromyl chloride, (2) sulphur trioxide, (3) carbonyl chloride, (4) sodium thiosulphate, (5) nickel carbonyl. (London Inter B Sc)

5 Describe the preparation and properties of nickel carbonyl, and state how the formation of this substance gives a commercial method for extracting nickel from its ores (London Inter)

6. Give an account of the "ammine" compounds of cobalt and platinum. Explain how the constitution of these compounds is usually represented, and show by diagrams that isomerism is possible. (London B Sc)

7. Write a short essay on *one only* of the following subjects. (*a*) Silicates. (*b*) Co-ordination compounds. (*c*) Hydrates.

ANSWERS TO QUESTIONS

Chapter I

3. 625 to 1.

Chapter V

1. 45·79 c.c., 0·06545 gm. **2.** 350·8 cu ft. **3.** 383·9 mm.
4. 53·42. **5.** 12·206 gm., 81·8 per cent
6. 0·0943 gm., 0·1772 gm **7.** 108·1. **8.** 37 3 lit.
9. 731 mm, H_2 542 mm, O_2 77 mm, N_2 112 mm

Chapter VI

2. 339 6 c c. 160·5 gm **4.** 0·00461 gm.
6. 0·728 gm. in water, 0·27₄ gm in ether

Chapters VII–VIII

2. 32·64. **3.** Ag = 107·92, S = 16·032. **4.** 32·48.
5. 42·5 per cent. C and 57·5 per cent O **6.** No.
9. 139 6 gm **10.** 118 litres
11. 251·3 gm ferrocyanide, 353 gm sulphuric acid, 61 gm water.

Chapter IX

1. 579 gm
2. 1·798, 2·326 gm per lit, C_2N_2; 2 lit. CO and 1 lit. N_2.
3. Cl_2 = 22·02 lit, CO_2 = 22·26 lit, NH_3 = 22·096 lit. **5.** 59·0.
7. 55·92, XCl_2 **8.** 57·3
9. 48 9 per cent, PCl_5 = 0 343 atm, $PCl_3 = Cl_2$ = 0·328 atm.
10. XO_2, X_2O_3. **11.** 119 [X_4S_7] **12.** D = 82·6, γ = 0 5375.
15. At. wt = 236·2 (H = 1), XCl_4
16. (i) 1 to 3 0033; 13·896 (H = 1); (ii) 13·891 (H = 1). **20.** 28·018
21. 114·9; XCl, XCl_2, XCl_3 **22.** 205·2 **23.** 0·726

Chapter X

4. (*a*) 5·484 lit, (*b*) 9·597 lit.
5. 24·45 c c. at S T.P.; 47·24 per cent O_2 and 52·76 per cent. N_2, by vol.

Chapter XI

3. 3·79 c.c. **4.** 14·003; 44·003.

Chapter XIII

9. 2.

Chapter XV

3. 1 to 0 586. **5.** Density = 14·3 (O = 16) or 14·04 (H = 1).

Chapter XVI

3. 0·357 gm , 39·8 c c **4.** $\alpha = 0{\cdot}845$, $[H^{\cdot}] = 0{\cdot}342N$.
5. XCl_3 **7.** 282 c c. **8.** $\alpha = 0{\cdot}839$. **10.** 5 36 gm.
11. 1·357 gm. **12.** 2 **14.** 0·2835 gm , 0·0567 gm

Chapter XVII

2. 260·7 ; probably undissociated **3.** 364 **4.** 0·883 , 87·4.
5. 0 565 **7.** 62 **10.** 54 **12.** 30 **13.** 342·5.
15. 108·2. **18.** 129·7. **19.** 346 **21.** 0·755.

Chapter XVIII

1. 7·5 c.c. **6.** Volume becomes 168 c c

Chapter XIX

6. 27·2 gm. ; 1·60N , 8·96 vols

Chapter XX

7. 0·191 ; 0·0955 **9.** 59·44 cm.
11. $\gamma = 0$ 683 , $K = 0$ 007915 , 477 mm **20.** 10^{-10}, $2{\cdot}33 \times 10^{-7}$ gm /lit

Chapter XXI

6. 48 k cal
7. (*a*) 335·35 k cal , (*b*) 334 19 k cal (*N.B.*—Heat equivalent of external work = $RT = 2T$ g cal per mol diminution in volume.)
9. 45 3 k cal. **10.** 37·03 k. cal **11.** 29 k. cal.
12. −12·4 k cal , −20·2 k cal , −8·7 k cal
19. 49·7 k. cal. (Note the thermochemical symbols used in the question)

Chapter XXIII

1. 27·09 **2.** 0·163 **3.** 63·5(H = 1·008); 31·75(O = 8); 63·5(O = 16).
4. 85·5.

Chapter XXIX

5. 1·7 gm. , 0·1N.

Chapter XXX

5. N_2O. **16.** 111·5 gm.

Chapter XXXIII

1. 77·5 , AsH_3.

Chapter XXXIV

4. CH_4 66·92, C_2H_6 19·44, H_2 13·64.
7. 12·5 H_2, 7·5 CH_4, 80 N_2 by vol. **18.** CH_4.

Chapter XXXVI

8. 10·94.

Chapter XXXIX

13. 995·2 c.c.

Chapter XLII

12. 79.

Chapter XLVIII

2. 44·26. 8. 0·948 gm 9. 6·954 gm. ; 11·36 c.c.

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