PART II

THE STUDY OF FOUR TYPICAL ELEMENTS

HYDROGEN—OXYGEN—NITROGEN—CARBON

AND THEIR MORE IMPORTANT COMPOUNDS

CHAPTER I

HYDROGEN

Symbol, H. Atomic weight = 1.01. Molecular weight = 2.02. Density = 1.01.

History.—The existence of hydrogen as an individual substance was first established by Cavendish (1766), who applied to it the name *inflammable air*. He obtained the gas by acting upon certain metals, as iron, tin, and zinc, with either sulphuric or hydrochloric acid.

Occurrence.—In the free state hydrogen occurs only in small quantities upon the earth. It is evolved with other volcanic gases, and is present in the gases which escape from petroleum wells. It is evolved also during the fermentation and decomposition of certain organic compounds, and is therefore present in the breath and the intestinal gases of animals. From these sources it finds its way into the atmosphere, where it is present to the extent of about .2 volumes in 1000 volumes of air. Hydrogen has also been found in many specimens of meteoric iron, and also in certain rocks, where it is present as *occluded* gas.

Hydrogen in the uncombined state exists in enormous masses upon the sun, and is present in certain stars and nebulæ. The so-called *prominences* which are seen projecting from the sun's disk to a distance of many thousands of miles, and which were first observed during solar eclipses, consist of vast masses of incandescent hydrogen.

In combination with other elements hydrogen is extremely abundant; its commonest compound is water, which consists of one part by weight of this element combined with eight parts of oxygen. In combination with chlorine, as hydrochloric acid, with carbon as marsh gas, and with sulphur as sulphuretted hydrogen, this element also occurs in large quantities. All known acids contain hydrogen as one of their constituents, and it is present in almost all organic compounds.

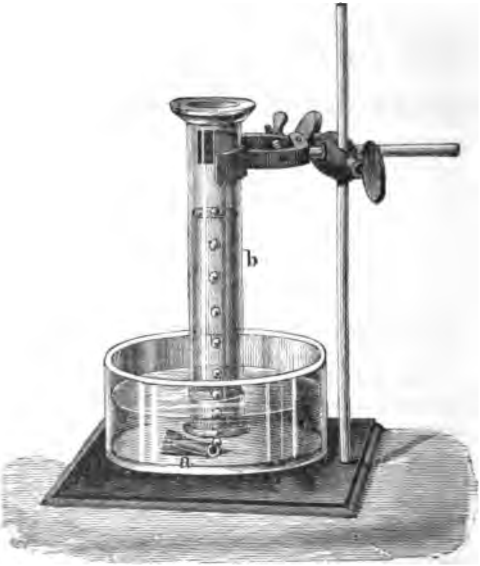

FIG. 27.

Modes of Formation.—(1.) Hydrogen may be obtained from water by the action of various metals upon that compound under certain conditions. The metals sodium and potassium will decompose water at the ordinary temperatures; when, therefore, a fragment of either of these metals is thrown upon water, the latter is decomposed and hydrogen set free :—

$$H_2O + Na = NaHO + H.$$

The metals, being lighter than water, float upon its surface, and, owing to the heat of the reaction, melt and roll about upon the liquid as molten globules. With potassium, the heat developed is sufficiently great to cause the hydrogen to inflame, and it burns with a flame coloured violet by the vapour of the metal. The hydroxide of the metal, which is the second product of the action, dissolves in the excess of water, rendering the liquid alkaline. The alkalinity of the solution may be made evident by the addition of a reddened solution of litmus, which will be turned blue by the alkali.

In order to collect the hydrogen evolved by the action of sodium upon water, the metal is placed in a short piece of lead tube closed at one end, which causes it to sink in the liquid, and an inverted glass cylinder filled with water is placed over it, as shown in Fig. 27. The evolved hydrogen then rises as a stream of bubbles into the cylinder and displaces the water.*

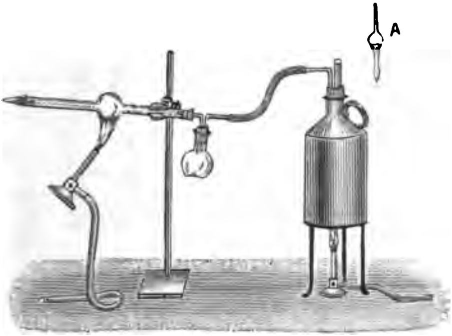

FIG. 28.

(2.) Water may be readily decomposed at the boiling-point, by means of zinc, if the metal be previously coated with a thin film of copper by immersion in a dilute solution of copper sulphate. When this copper-coated zinc (known as zinc-copper couple) is heated in a small flask filled with water, and provided with a delivery tube, the oxygen of the water combines with the zinc forming zinc oxide, and hydrogen is evolved, which may be collected over water at the pneumatic trough :*—

$$Zn + H_2O = ZnO + H_2.$$

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* For detailed description of these experiments, see Newth's "Chemical Lecture Experiments," p. 2.

(3.) At a still higher temperature, water in the state of steam can be readily decomposed by the metal magnesium, magnesium oxide being formed and hydrogen liberated :—

$$Mg + H_2O = MgO + H_2.$$

For this purpose the magnesium is strongly heated in a glass bulb (Fig. 28), while steam from a small boiler is passed over it. As the temperature of the metal approaches a red heat it bursts into flame, and the issuing hydrogen may be ignited as it escapes from the end of the tube.

(4.) If iron be heated to bright redness and steam be passed over it, the water is decomposed, the oxygen uniting with the iron to form an oxide known as triferric tetroxide, or ***magnetic oxide of iron***, thus—

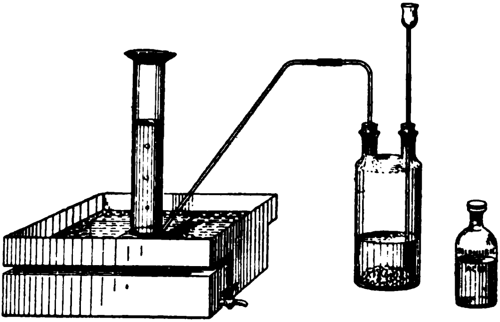

FIG. 29.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

This method is employed on a large scale for the preparation of hydrogen for commercial purposes. Iron borings or turnings are packed into an iron tube, which is strongly heated in a furnace, and steam from a boiler is passed through the tube.

(5.) For laboratory purposes hydrogen is most conveniently prepared by the action of dilute sulphuric acid upon zinc :—

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

For this purpose granulated zinc (*i.e.* zinc which has been melted and poured into water) is placed in a two-necked Woulf's bottle (Fig. 29), and a quantity of sulphuric acid, previously diluted with six times its volume of water, is introduced by means of the funnel. A brisk action sets in, and hydrogen is rapidly disengaged. After the lapse of a few minutes the air within the apparatus will be swept out by the hydrogen, when the gas may be collected over water in the pneumatic trough.

The hydrogen so obtained is never absolutely pure; it is liable to contain traces of arsenic hydride, hydrogen sulphide, hydrogen phosphide, oxides of nitrogen, and nitrogen. The nitrogen is derived from the air, which finds its way through joints in the apparatus, and also from air dissolved in the acid. There is no known process for removing this impurity. The other gases are due to impurities in the zinc and the sulphuric acid, and can be removed, if required, by passing the hydrogen through a series of tubes containing absorbents (see page 210).

Absolutely pure sulphuric acid, even when diluted with water, has no action upon perfectly pure zinc.

Scrap iron may be substituted for zinc, but the hydrogen so obtained is much less pure, and is accompanied by compounds of carbon (derived from the carbon in the iron), which impart to the gas an unpleasant smell; the reaction in this case is the following:—

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Hydrochloric acid can be employed in place of sulphuric acid with either zinc or iron, the reaction then being:—

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

These actions of acids upon metals when expressed in the form of ionic equations will each be seen to consist simply of the transference of two positive atomic charges from two hydrogen ions to an atom of the metal, whereby the latter is converted into a divalent ion, thus—

$$Zn + 2H^{\cdot} + 2Cl' = H_2 + Zn^{\cdot\cdot} + 2Cl'.$$

(6.) Hydrogen in a high degree of purity is conveniently prepared in small quantity by the electrolysis of water acidulated with sulphuric acid (see page 207).

(7.) Hydrogen is disengaged when certain metals, such as zinc, iron, and aluminium, are boiled with an aqueous solution of potassium or sodium hydroxide. Thus, in the case of zinc, when this metal in the form of filings is boiled with a solution of potassium hydroxide, hydrogen is evolved, and a compound of zinc, potassium, and oxygen remains in solution, namely, potassium zinc oxide (or potassium zincate), thus:—

$$2KHO + Zn = H_2 + ZnK_2O_2.$$

(8.) Hydrogen is also obtained by heating alkaline oxalates, or formates, with either potassium or sodium hydroxide, with the simultaneous formation of an alkaline carbonate; thus with sodium oxalate:—

$$Na_2C_2O_4 + 2NaHO = H_2 + 2Na_2CO_3.$$

Properties.—Hydrogen is a colourless gas, and has neither taste nor smell. It is the lightest known substance, being 14.3875 times lighter than air. Its specific gravity is 0.0695 (air = 1). One litre of the gas at 0° C., and under a pressure of 760 mm. of mercury (*i.e.* the standard temperature and pressure) weighs 0.089873 gramme; or 1 gramme of hydrogen at the standard temperature and pressure occupies 11.127 litres.

On account of its extreme lightness, hydrogen may be poured *upwards* from one vessel to another. If a large beaker be suspended mouth downwards from the arm of a balance and counterpoised, and the contents of a jar of hydrogen be poured upwards into the beaker, the equilibrium of the system will be disturbed, and the arm carrying the beaker will rise.

FIG. 30.

The lightness of hydrogen can also be shown by causing a stream of the gas to issue from a tube placed in such a position that its shadow is cast upon a white screen by means of a powerful electric light. When the gas is streaming from the tube, its upward rush will be visible upon the screen as a distinct shadow, caused by the difference between the refractive power of air and hydrogen (Fig. 30).

Hydrogen is inflammable and burns with a non-luminous flame, the temperature of which is very high. The product of the combustion of hydrogen is water, and if a jet of the gas be burned beneath the apparatus seen in Fig. 31, considerable quantities of water may be collected in the bulb. In the act of combustion the hydrogen combines with the oxygen of the air, forming the oxide of hydrogen, namely, water:*—

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

If hydrogen be mixed with the requisite quantity of air, or oxygen, and a light applied to the mixture, the combination of the two gases takes place instantly with a violent explosion;† hence the necessity of carefully expelling all the air from the apparatus in which hydrogen is being generated before applying a flame to the issuing gas.

Hydrogen will not support the combustion of ordinary combustibles; thus, if a burning taper be thrust into a jar of the gas, the hydrogen itself will be ignited at the mouth of the jar, which must be held in an inverted position, but the taper will be extinguished; on withdrawing the taper it may be re-ignited by the burning hydrogen.

Although hydrogen is not poisonous, it is incapable of supporting animal life owing simply to the exclusion of oxygen. When mixed with air and inhaled, it raises the pitch of the voice

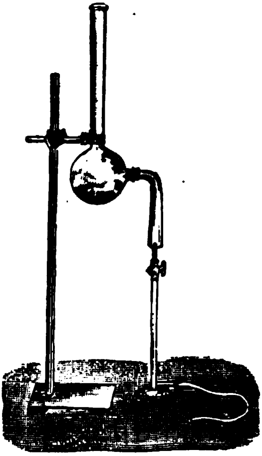

FIG. 31.

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* From this fact the name Hydrogen (signifying *the water producer*) is derived.

† Baker has recently shown (*Jour. Chem. Soc.*, April 1902) that if the two gases are *perfectly pure and dry*, they may be strongly heated without uniting. In these experiments a coil of silver wire suspended in the gases was heated by means of an electric current until the silver melted, that is, above 1000°; but no chemical union of the oxygen and hydrogen took place, although the ordinary temperature of explosion is 615° (V. Meyer). Baker has also shown that if a mixture of these two gases, which has not been specially dried, be exposed to sunlight, combination *slowly* takes place; whereas with the perfectly dry gases no measurable combination occurs.

almost to a falsetto. The same effect may be seen by sounding a pitch-pipe, or organ-pipe, by means of a stream of hydrogen instead of ordinary air, when it will be noticed that the note given out is greatly raised in pitch.

Hydrogen is very slightly soluble in water. It was formerly believed that this gas formed an exception to the rule that the solubility of gases in water diminishes with rise of temperature, and it was supposed that the solubility of hydrogen was constant between the temperatures 0° and 25°. More recent experiments have shown that this is not the case. The solubility of this gas, as determined by W. Timofejeff (1890), is seen in the table on p. 143.

Hydrogen was first liquefied on May 10, 1898, by Dewar. Prior to this time it had never been obtained as a coherent or static liquid—that is, a liquid with a meniscus—although momentary indications of its liquefaction had been obtained by Olszewski as far back as 1895. The critical temperature of hydrogen (namely, −238°) being below the lowest point obtainable by the rapid ebullition of liquid oxygen or air, no external refrigerating agent is available which is capable of cooling the gas below its critical point, and therefore of causing its liquefaction. By an extension of the principle of self-cooling explained on p. 76, however, namely, by causing a jet of the gas previously cooled to −205° to continuously escape from a fine orifice under a pressure of 180 atmospheres, Dewar has succeeded in collecting considerable quantities of liquid hydrogen in specially constructed vacuum-jacketed vessels.

Liquid hydrogen is clear and colourless as water, thus disposing of the theory once advocated that if obtained in the liquid state hydrogen would be found to exhibit metallic properties. The boiling-point of the liquid is −253° (Dewar), at which temperature air is immediately solidified. Thus, if a tube sealed at one end, but freely open to the air at the other, be immersed in liquid hydrogen, the cooled end of the tube quickly becomes filled with solidified air. Similarly, oxygen is frozen to a pale-blue solid.

The specific gravity of liquid hydrogen is about 0.07; that is to say, it is only about $\frac{1}{14}$th the density of water, or about 14 c.c. of the liquid weighs only 1 gramme. By its own rapid evaporation liquid hydrogen has been frozen to a white solid mass, which melts at −257°; and by the rapid evaporation of this solid a temperature of −260° has been obtained, which is the lowest degree of cold ever reached. By means of liquid hydrogen as a refrigerating agent, the more recently discovered gas Helium has also been liquefied (see p. 269), hence all the known gases have now been condensed to the liquid state.

Occluded Hydrogen, or Hydrogenium.—Certain metals, such as iron, platinum, and notably palladium, possess the property when heated of absorbing a large quantity of hydrogen, and of retaining it when cold. Graham found that at a red heat palladium absorbed, or *occluded*, about 900 times its own volume of hydrogen, while even at ordinary temperatures it was able to absorb as much as 376 times its volume.* Graham concluded that the hydrogen so occluded assumed the solid form, and was alloyed with the palladium, and to denote the metallic nature of the gas he gave to it the name *hydrogenium.* From later experiments of Troost and Hautefeuille, it seems probable that a definite compound of hydrogen and palladium exists, of the composition of Pd_2H.

After its absorption of hydrogen the metal presents the same appearance as before, although some of its physical properties have become slightly modified; thus it is more magnetic than ordinary palladium, and its electric conductivity is considerably reduced.

In view of our present knowledge of the entire absence of any metallic characters in liquid or solid hydrogen (gained, however, entirely since Graham's time), the view that this is an *alloy* is no longer tenable, as this term is only strictly applicable to the union of *metals.*

The absorption of hydrogen by palladium is readily seen by making a strip of palladium foil the negative electrode in an electrolytic cell containing acidulated water, the positive pole being of platinum. Oxygen will be evolved from the latter electrode, while for some time no gas will be disengaged from the surface of the palladium, the hydrogen being completely absorbed by the metal. During the absorption of hydrogen the palladium undergoes an increase in volume: Graham observed the increase in length of a palladium wire to be equal to 1.6 per cent.

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* According to Neumann and Strientz (*Zeitschrift für Analytische Chemie*, vol. 32), one volume of various metals in a fine state of division is capable of absorbing the following amounts of hydrogen :—

Palladium, black	. 502.35 vols.	Nickel . . .	. 17.57 vols.
Platinum, sponge	. 49.3 ,,	Copper . . .	4.5 ,,
Gold . . .	. 46.3 ,,	Aluminium . .	2.72 ,,
Iron . . .	. 19.17 ,,	Lead	0.15 ,,

This change in volume suffered by the metal may be strikingly demonstrated by employing two strips of palladium foil, protected on one side by a varnish, as the electrodes in the electrolytic cell. On passing the current the negative electrode immediately begins to bend over towards the varnished side: when the current is reversed it again uncurls; and the other, being now the negative pole, at once begins to perform the same curling movements.

Hydrogen, which is thus occluded in the metal palladium, is capable of bringing about a number of chemical changes which ordinary hydrogen is unable to effect: thus, when a strip of hydrogenised palladium is immersed in a solution of a ferric salt, a portion of the iron is reduced to the ferrous state.*

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* See "Chemical Lecture Experiments," Nos. 27, 28, 29.

CHAPTER II

OXYGEN

Symbol, O. Atomic weight = 16.00. Molecular weight = 32.

History.—Oxygen was discovered by Priestley (1774). He obtained it by heating the red oxide of mercury (known in those days as *mercurius calcinatus, per se*) by concentrating the sun's rays upon it by means of a powerful lens. Priestley applied to the gas the name *dephlogistigated air.* Oxygen was independently discovered by Scheele. Scheele's discovery of oxygen was published in 1775, but recent research among his original papers has brought to light the fact that the discovery was actually made in 1773, prior therefore to Priestley's discovery. Scheele called the gas *empyreal air*, on account of its property of supporting combustion. Lavoisier subsequently applied to this gas the name "oxygene" (from ὀξύς, sour; and γεννάω, I produce), to denote the fact that in many instances the products obtained by the combustion of substances in the gas were endowed with acid properties. Oxygen, indeed, came to be regarded as an essential constituent of acids, and was looked upon as the "acidifying principle." The subsequent development of the science has shown that this idea is erroneous, and that oxygen is not a necessary constituent of all acids.

Occurrence.—In the free state oxygen occurs in the atmosphere, mechanically mixed with about four times its volume of nitrogen. In combination with other elements it is found in enormous quantities. Thus it constitutes eight-ninths by weight of water, and nearly one-half by weight of the rocks of which the earth's crust is mainly composed.

The following table (Bunsen) gives the average composition of the earth's solid crust, so far as it has been penetrated by man. It must be remembered, however, that the greatest depth to which man has examined, when compared with the diameter of the earth, is after all only, as it were, a mere scratch.

Average Composition of the Earth's Crust.

Oxygen	44.0	to	48.7
Silicon	22.8	„	36.2
Aluminium	9.9	„	6.1
Iron	9.9	„	2.4
Calcium	6.6	„	0.9
Magnesium	2.7	„	0.1
Sodium	2.4	„	2.5
Potassium	1.7	„	3.1
	100.00		100.00

Modes of Formation.—(1.) Oxygen may readily be obtained by a slight modification of Priestley's original method, namely, by heating mercuric oxide in a glass tube, by means of a Bunsen flame. The red oxide of mercury first darkens in colour, and is decomposed by the action of the heat into mercury and oxygen, thus—

$$2HgO = 2Hg + O_2.$$

The evolved oxygen may be collected over water in the pneumatic trough, while the mercury condenses in the form of metallic globules upon the cooler parts of the tube. This method of obtaining oxygen is never employed when any quantity of the gas is required—it is chiefly of historic interest.

(2.) For experimental purposes oxygen is best prepared from potassium chlorate. When this salt is heated it melts, and at about 400° decomposes with brisk effervescence due to the evolution of oxygen, while potassium chloride remains :*—

$$KClO_3 = KCl + 3O.$$

If the potassium chlorate be previously mixed with about one-fourth of its weight of manganese dioxide, it gives up the whole of its oxygen at a temperature considerably below the melting-point of the salt, and at a greatly accelerated rate. When, therefore, the oxygen is not required to be perfectly pure, a mixture of these two

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* The mechanism of this reaction is more complex than is represented by this equation. It has been shown (P. F. Frankland) that during the decomposition potassium perchlorate, $KClO_4$, is continuously being formed, and again resolved into $KClO_3$ and O. The extent to which this takes place depending upon the temperature.

substances is usually employed. The mixture may be conveniently heated in a "Florence" flask, supported in the position shown in the figure, and gently heated with a Bunsen flame. The gas is washed by being passed through water, and then collected either at the pneumatic trough or in a gas-holder.

The manganese dioxide is found at the end of the reaction to be unchanged: the part it plays in the decomposition belongs to a class of phenomena to which the name *catalysis* is applied; the manganese dioxide, in this instance, being the *catalytic agent.* It was at one time supposed that by its mere presence, itself undergoing no change, the manganese dioxide enabled the potassium chlorate to give up its oxygen more readily and at a lower temperature; but the accumulated evidence which has been collected by the study of an increasing number of similar cases of catalytic action leads to the conclusion that the manganese dioxide is here playing a more distinctly chemical part in the reaction. So far as is known, in all phenomena of this order, the catalytic agent is a substance which possesses a certain degree of chemical affinity for one of the constituents of the body to be decomposed, and the influence of this attraction is a necessary factor in determining the splitting up of the compound. Owing, however, to certain conditions which are present, such, for example, as the particular temperature at which the reaction is conducted, the catalytic agent is unable to actually combine with the constituent for which it has this affinity, or if it combines, the combination it forms is unable to exist and is instantly resolved again: hence the catalytic agent comes out of the action in the same state as it was at the commencement.

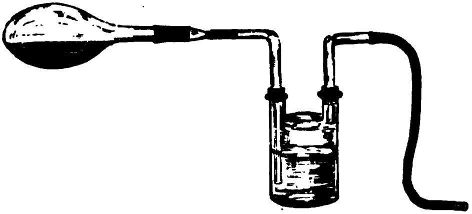

FIG. 32.

In the case before us, it is now believed* that the action of the manganese dioxide in facilitating the evolution of oxygen from

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* Sodeau, *Trans. Chem. Soc.*, 1902, vol. ii. p. 1066.

potassium chlorate is due to the formation of a higher oxide of manganese by the oxidising action of the chlorate, which oxide being unstable under the existing conditions, subsequently breaks up into oxygen and the original oxide.*

The temperature at which this reaction takes place is below that which is necessary for the formation of potassium perchlorate, hence under these conditions this salt is not produced.

(3.) When manganese dioxide itself is heated to bright redness, it parts with one-third of its oxygen and is converted into trimanganic tetroxide.

$$3MnO_2 = Mn_3O_4 + O_2.$$

(4.) Other peroxides, when heated, similarly yield a portion of the oxygen they contain. One of these, namely, barium peroxide, is now largely employed for the preparation of oxygen upon a manufacturing scale. This method, known as *Brin's* process, from the name of the inventor, is based upon the fact that when barium oxide (BaO) is heated in contact with air, it unites with an additional atom of oxygen, forming barium peroxide, thus—

$$BaO + O = BaO_2.$$

And that when this substance is still further heated, it again parts with the additional oxygen and is reconverted into the monoxide—

$$BaO_2 = BaO + O.$$

The process, therefore, is only an indirect method of obtaining oxygen from the air, the same quantity of barium monoxide being employed over and over again. In practice it was found that instead of effecting the two reactions by altering the temperature, which involved loss of time and considerable expense, the same result could be obtained by altering the *pressure* and keeping the temperature constant. If the monoxide be heated to the lower temperature, at which the first reaction takes place, and air be passed over it at the ordinary atmospheric pressure, atmospheric oxygen is taken up and barium peroxide is formed. If the pressure

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* Secondary reactions simultaneously take place, resulting in the formation of small quantities of potassium permanganate, and the evolution of traces of chlorine.

be then slightly reduced by suitable exhaust pumps, the peroxide immediately gives up one atom of oxygen without any further application of heat, and is retransformed into the monoxide. In

General Plan of Oxygen-producing Plant

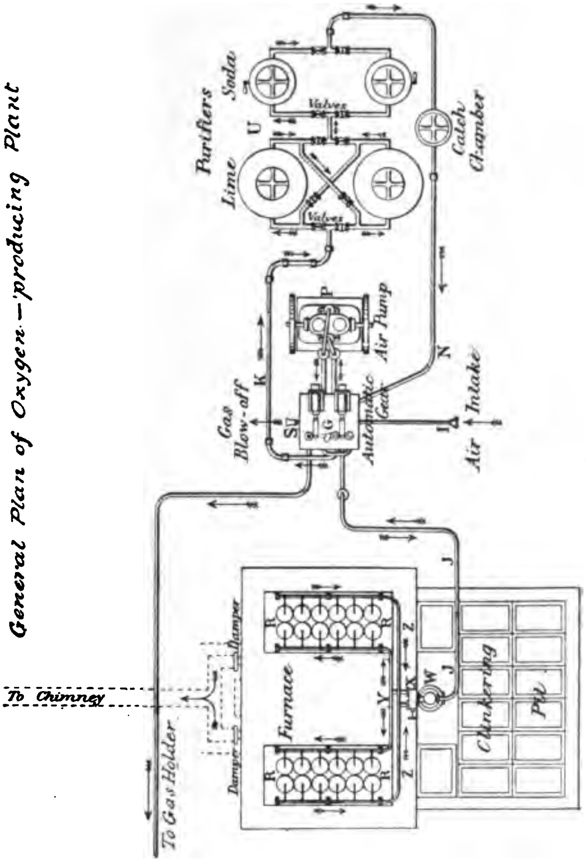

FIG. 33

this way, by alternately sending air through the heated retorts containing the oxide and then exhausting the retorts, a continuous process is obtained without change of temperature.

The *modus operandi* of the process will be seen from Fig. 33, which represents the general arrangement of the apparatus. A number of retorts, R, consisting of long narrow iron pipes, are arranged vertically in rows in the furnace, where they are heated by means of "producer-gas" (*i.e.* carbon monoxide with atmospheric nitrogen, obtained by the regulated combustion of coke).

By means of the pump P, air is drawn in at the "air intake," and forced through purifiers in order to withdraw atmospheric carbon dioxide; the complete removal of this impurity being essential to the successful carrying out of the operation. The purifiers are so arranged that any of them can be thrown out of use at will.

By means of automatic gear the purified air is sent through pipe J to the distributing valve X, from which it passes by the pipe Y into the retorts, being made to pass down through one row and up through the other. The oxygen is then absorbed, and the accumulating nitrogen escapes by the relief valve W. When the absorption of oxygen by the barium monoxide in the retorts has continued for ten or fifteen minutes, the automatic reversing gear comes into operation. The relief valve W is thereby closed, communication with the purifiers is cut off, and the action of the pumps at once causes a reduction of pressure within the retorts. When the pressure falls to about 660 mm. (26 inches, or about 13 lbs. on the square inch), the peroxide gives up oxygen, and is reduced to the monoxide. The oxygen is drawn away by the pipe J and is passed on to a gas-holder. The first portions of gas that are drawn out of the retorts will obviously be mixed with the atmospheric nitrogen which was there present; in order that this shall be got rid of, the automatic gear is so arranged that communication with the pipe leading to the gas-holder is not opened until a few seconds after the reversing gear is in operation, and the first portions of gas that are pumped out are made to escape into the air by a snifting valve S, which is automatically opened and closed.

(5.) Oxygen may be obtained by heating manganese dioxide with sulphuric acid, the dioxide parting with the half of its oxygen, and a sulphate of the lower oxide being formed—*

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

(6.) Similarly, potassium dichromate (a salt containing chromium

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* In order to avoid unnecessarily complicating chemical equations, it is sometimes convenient to represent them atomically. Moreover, by so doing the mechanism of the reaction is often rendered more clear.

trioxide, CrO_3), when heated with sulphuric acid, yields oxygen; the chromium at the same time being reduced to a lower state of oxidation, viz., Cr_2O_3, in which condition it unites with sulphuric acid, forming chromium sulphate—

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

During the reaction the red colour of the dichromate changes to the deep olive-green colour possessed by chromium sulphate.

(7.) Many other highly oxidised salts yield oxygen when acted upon by sulphuric acid; thus, with potassium permanganate the following action takes place:—

$$K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

(8.) If hydrogen peroxide be added to dilute sulphuric acid, and the mixture dropped upon a solution of potassium permanganate contained in a suitable generating flask, a rapid evolution of oxygen takes place at the ordinary temperature, thus—

$$K_2Mn_2O_8 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

(9.) When strong sulphuric acid is dropped upon fragments of brick or pumice-stone, contained in an earthenware or platinum retort and maintained at a bright red heat, the acid is decomposed into water, sulphur dioxide, and oxygen—

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

The products of the decomposition are passed through water, which absorbs the sulphur dioxide, and also arrests any undecomposed sulphuric acid, and the oxygen is collected over water. When this process is used on a large scale, the sulphur dioxide is absorbed by being passed through a tower filled with coke, and down which a stream of water is allowed to trickle, and the solution so obtained can be utilised in the manufacture of sulphuric acid.

(10.) Oxygen can be obtained from bleaching-powder by methods which afford interesting instances of catalytic action.* The composition of bleaching-powder is expressed by the formula $Ca(OCl)Cl$. If this substance be mixed with water, and a small quantity of precipitated cobalt oxide added, and the mixture gently warmed, oxygen is rapidly evolved. The cobalt oxide, CoO, is the catalytic agent; it is able to combine with more oxygen to form

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* Experiments 35, 36, 37, 152, "Chemical Lecture Experiments," new ed.

Co_2O_3, but this compound is reduced as fast as it is formed, and the oxygen is evolved as gas—

(1) $$Ca(OCl)Cl + 2CoO = Co_2O_3 + CaCl_2.$$
(2) $$Co_2O_3 = 2CoO + O.$$

A solution of calcium hypochlorite, which may be obtained from bleaching-powder (see Bleaching-powder), behaves in the same way; and, as in the above reaction, nickel oxide may be substituted for cobalt—

$$Ca(OCl)_2 = CaCl_2 + O_2.$$

(11.) A similar instance of catalysis, by which oxygen may be obtained, is seen when a stream of chlorine gas is passed through boiling milk of lime, to which a small quantity of the oxide of cobalt or nickel has been added—

$$CaH_2O_2 + Cl_2 = CaCl_2 + H_2O + O.$$

A reaction of the same order takes place when the milk of lime is replaced by either potassium or sodium hydroxide—

$$2NaHO + Cl_2 = 2NaCl + H_2O + O.$$

(12.) When a mixture of steam and chlorine gas is heated to bright redness, the steam is decomposed, the hydrogen combining with the chlorine to form hydrogen chloride (hydrochloric acid), and the oxygen is set free—

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

In order to prepare oxygen by this reaction, chlorine gas is caused to bubble through water which is briskly boiling in a glass flask, F (Fig. 34). The mixture of chlorine and steam is then passed through a porcelain tube filled with fragments of porcelain, and maintained at a bright red heat in a furnace. The issuing gases are passed through a Woulf's bottle, containing a solution of sodium hydroxide, in order to absorb the hydrochloric acid, and the oxygen is collected at the pneumatic trough.

(13.) Oxygen is formed on a large scale in nature by the decomposition of atmospheric carbon dioxide by the green leaves of plants, under the influence of light. The carbon dioxide is decomposed into carbon, which is assimilated by the plant, and into oxygen, which is thrown into the atmosphere. It has been estimated that 1 square metre of green leaf is able, under the influence of sunlight, to decompose more than 1 litre of carbon dioxide per hour.

(14.) Of the many other methods by which it has been proposed, from time to time, to manufacture oxygen on a large scale, may be mentioned one, known as the Tessié du Motay process, from the name of the inventor. This method consists in the alternate formation and decomposition of sodium manganate. The process consists of two operations, which are carried out at different temperatures. When a current of air is passed over a moderately heated mixture of manganese dioxide and sodium hydroxide, sodium manganate is formed—

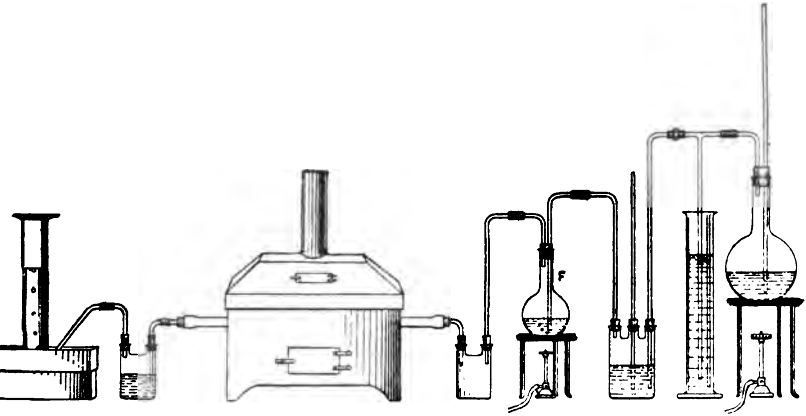

FIG. 34.

$$2MnO_2+4NaHO+O_2=2H_2O+2Na_2MnO_4.$$

And if this sodium manganate be heated to bright redness, and a current of steam at the same time passed over it, the manganate is reduced to dimanganic trioxide, sodium hydroxide is reformed, and oxygen evolved, thus—

$$2Na_2MnO_4+2H_2O=Mn_2O_3+4NaHO+3O.$$

On again passing air over the residue, after allowing the temperature of the mass to fall to that at which the first reaction was conducted, sodium manganate is once more reformed—

$$Mn_2O_3+4NaHO+3O=2H_2O+2Na_2MnO_4.$$

Properties.—Oxygen is a colourless gas, having no taste or smell. It is slightly heavier than air, its specific gravity being 1.1056 (air = 1). One litre of the gas, at the standard temperature and pressure, weighs 1.43028 grammes. Oxygen is slightly soluble in water. 1 c.c. of water at 0° C. dissolves 0.0489 c.c. of oxygen measured at 0° C. and 760 mm. pressure. The solubility of oxygen in water diminishes as the temperature rises in accordance with the interpolation formula (Winkler):—

$$c=0.0489-.0013413t+.0000283t^2-.00000029534t^3.$$

Fish are dependent upon the dissolved oxygen in water for their supply of this gas for respiration. Oxygen is also soluble in molten silver, which is capable of absorbing about twenty times its own volume of this gas (see Silver).

Oxygen is endowed with very powerful chemical affinities. Even at the ordinary temperature it is able to combine with such elements as phosphorus, sodium, potassium, and iron. All the chemical phenomena exhibited by the atmosphere are due to the presence in it of free oxygen, the atmosphere being practically oxygen diluted with four times its volume of nitrogen. Thus, when a piece of bright metallic sodium is exposed to the air, the surface becomes instantly tarnished and coated over with a film of oxide: when iron rusts, it in the same way is being acted upon by the oxygen of the air forming oxide of iron; in these cases the metals are said to become *oxidised.* If the metal be obtained in a sufficiently finely divided condition before being exposed to the air, or to pure oxygen, this process of oxidation may proceed so rapidly that the heat developed by the combination will cause the metal to burn. When the process of oxidation is accompanied by light and heat, the phenomenon is known as *combustion*, the oxygen being spoken of as the *supporter of combustion:* bodies which burn in the air, therefore, are simply undergoing rapid combination with oxygen. It will obviously follow, that bodies which are capable of burning in the air will burn with greatly increased rapidity and brilliancy when their combustion is carried on in pure or undiluted oxygen. A glowing chip of wood, or a taper with a spark still upon the wick, when plunged into pure oxygen, will be instantly rekindled. Such substances as sulphur, charcoal, phosphorus, which readily burn in air, when burnt in pure oxygen carry on their combustion with greatly increased brilliancy. Many substances which are not usually regarded as combustible bodies will burn in oxygen if their temperature be raised sufficiently high to initiate the combustion; thus a steel watch-spring, or a bundle of steel wires, if strongly heated at one end, will burn in oxygen, throwing out brilliant scintillations. This experiment is most readily shown by projecting a spirit-lamp flame upon the ends of a bundle of steel wire, by means of a stream of oxygen, as shown in Fig. 35. As soon as the ends of the wire are sufficiently heated, and begin to burn, the lamp may be withdrawn and the wire held in the issuing stream of oxygen, in which it will continue its combustion with great brilliancy.*

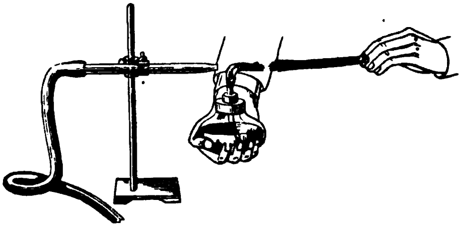

FIG. 35.

It is a remarkable fact, and one which has not yet received any entirely satisfactory explanation, that these instances of combustion in oxygen will not take place if both the gas and the material be *absolutely* dry. It has been shown that phosphorus, sealed up in a tube with oxygen which has been absolutely freed from aqueous vapour, may even be distilled in the gas without any combination taking place. A mixture of oxygen and carbon monoxide, which under ordinary circumstances explodes when heated, is found when perfectly dry to remain unaffected by the passage of an electric spark (p. 298). Similarly, perfectly dry chlorine is without action upon metals such as copper or sodium, while under common conditions it combines with them with the greatest readiness. In all these cases where the absolutely dry materials are incapable

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* See also Experiments 48–52, "Chemical Lecture Experiments."

of acting upon each other, the introduction of the minutest trace of moisture is sufficient to allow the action to proceed, but the exact way in which this operates in causing the effect is at present not known with certainty.*

Oxygen is the only gas which is capable of supporting respiration: an animal placed in any gas or gaseous mixture containing no free oxygen rapidly dies. Undiluted oxygen may be breathed with impunity for a short time, but its continued inhalation soon produces febrile symptoms. The inhalation of oxygen is occasionally had recourse to in cases of asphyxiation, or under

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* It would seem evident if it is the presence of water, and *water only* as the third substance, which is the necessary condition to bring about chemical action in such cases as these, that however completely a mixture of oxygen and *hydrogen* were dried, it would explode when heated above the temperature at which union begins; because the product of the combination of a minute portion of the mixture would furnish sufficient water to determine the explosion of the remainder. The researches of V. Meyer, Dixon, and Baker, extending over the last decade, seemed to entirely confirm this view, for they could detect no diminution in the velocity of the union of these gases even when most carefully dried.

Quite recently, however (April 1902), Baker has shown that if these gases be perfectly *pure* (see p. 208), as well as perfectly *dry*, the mixture may be heated to temperatures much higher than that at which combination usually takes place without exploding. Moreover, if the pure gases are heated before the drying operation has been carried to its highest degree, it is found that although union begins to take place and water is actually formed in quantity greatly in excess of that which would be necessary to bring about the action had the gases *not* been pure, nevertheless no explosion of the mixture takes place. The gases being absolutely pure to start with, the water produced by their union will also be pure; and it would appear from these experiments that perfectly pure water alone is not capable of bringing about these chemical combinations.

These new and most interesting results lend support to the hypothesis which has been put forward in order to explain the influence of water in determining such chemical actions as these, namely, that chemical action cannot take place without the presence of an electrolyte; that the removal of water is in reality the removal of any possibility of an electrolyte being present. If the water present is absolutely pure, since pure water is a non-electrolyte (p. 109), it should therefore not be able to operate in causing the chemical action to take place. On the other hand, any impurity present in the water would at once cause it to become an electrolyte, in which case it would be able to bring about the chemical action.

Experiments have been made with a view to determine whether or not the gases themselves undergo any dissociation in the moist condition or during the process of drying. But the results so far only show that if any dissociation takes place, the extent to which it occurs is beyond the limits of measurement by any volumetric methods.

circumstances of great bodily prostration, where the necessary oxygenation of the blood cannot take place on account of the enfeebled action of the lungs.

Compressed oxygen acts upon the animal economy as a poison : an animal placed in oxygen gas under a pressure of only a few atmospheres quickly dies.

During the respiration of man, air is drawn into the lungs, and is there deprived of 4 to 5 per cent. of its oxygen, and gains 3 to 4 per cent. of carbon dioxide. The oxygen that is withdrawn from the inhaled air by means of the lungs is absorbed by the blood. The power to absorb this oxygen is believed to reside in a crystalline substance contained in the corpuscles of the blood, called *hæmoglobin*, with which it enters into feeble chemical union, forming the substance known as *oxyhæmoglobin*. This substance is red, and imparts to arterial blood its well-known colour. During its circulation in the system the oxyhæmoglobin parts with its oxygen, and is reconverted into the purple-coloured hæmoglobin. Under normal conditions the whole of the oxyhæmoglobin is not so reduced, for venous blood is found still to contain it to some extent. The amount of carbon dioxide exhaled is diminished during sleep, and to a still greater extent during hibernation.

Oxygen can be liquefied at very low temperatures by the application of moderate pressure (see Liquefaction of Gases). It was first liquefied in 1877 by Cailletet, and independently by Pictet. Its critical temperature is −118.8°, at which point a pressure of 58 atmospheres is required to bring about its liquefaction.

Liquid oxygen is a pale steel-blue, mobile liquid, which boils at −182.5°. Its specific gravity at −182.5° is 1.1315. The liquid expands when warmed much more rapidly than gases do for the same increment of temperature, and its density diminishes in proportion, thus—

At −182.5° density = 1.124.
„ −139° „ = .877.
„ −134° „ = .806.
„ −129° „ = .755.

Liquid oxygen is strongly magnetic. If a quantity of the liquid be placed in a dish between the poles of a powerful electro-magnet, the liquid will be drawn up to the magnet the instant the latter is excited.

ISOMERISM—POLYMERISM—ALLOTROPY.

Isomerism.—It is frequently found that two different compounds have the same composition; that is, their molecules are composed of the same number of the same atoms, and yet the substances have different properties. Such compounds are said to be *isomeric*, the one is an *isomer* of the other, and the phenomenon is called *isomerism*. Cases of isomerism are so numerous among the compounds of carbon (*i.e.* in the realm of organic chemistry, see Carbon, p. 295), that it has been found convenient to classify them. The term isomerism, therefore, is frequently restricted to cases in which the compounds have the same percentage composition, the same molecular weight, and belong to the same chemical type or class of substances. Thus, the two compounds dimethyl benzene and ethyl benzene are both expressed by the formula C_8H_{10}. The molecules in each case contain 8 atoms of carbon and 10 atoms of hydrogen, they therefore have the same molecular weight and the same percentage composition; and as they both belong to the same type or family, they are said to be isomeric with each other. The difference in the properties of these compounds is due to a difference in the arrangement of the atoms within the molecules, and this difference is expressed in their formulæ in the following manner:—

Dimethyl benzene, $C_6H_4(CH_3)_2$. Ethyl benzne, $C_6H_5(C_2H_5)$.

Different compounds having the same molecular weight and the same percentage composition, but which do not belong to the same family of compounds, are distinguished as *metamers*. Thus, the two compounds acetone and allyl alcohol are each expressed by the formula C_3H_6O. They have the same molecular weight and the same percentage composition, but belong to two widely different types of compounds; they are therefore called *metameric* compounds. The difference between them is again due to a difference in molecular structure, and they are distinguished by formulæ which convey this difference, thus:—

Acetone, $CO(CH_3)_2$. Allyl alcohol, $C_3H_5(HO)$.

Polymerism.—This term is employed to denote those cases in which different compounds belonging to the same family have the same percentage composition, but differ in molecular weight; that is to say, their molecules are composed of the same elements, which are present in the same *proportion;* but they do not contain the same actual numbers of the various atoms, and therefore have different weights. Thus, the compounds ethylene (C_2H_4), propylene (C_3H_6), butylene (C_4H_8), belong to the same family, and have each the same percentage composition, but they differ in molecular weight. These substances are said to be polymers of one another.

Allotropy may be regarded as a special case of polymerism. In its widest sense the term is sometimes used to denote polymerism in general, but it is usually restricted to those instances of polymerism which are exhibited by elementary bodies only. Many of the elements are capable, under special conditions, of assuming such totally different habits and properties, that they appear to be entirely different substances. Thus, the element sulphur, as usually seen, is a primrose-yellow, opaque, solid substance, extremely brittle, and readily dissolved by carbon disulphide. Under certain circumstances it may be made to appear a totally different thing; it is then a translucent amber-coloured substance, soft and elastic like indiarubber, and insoluble in carbon disulphide; it is still sulphur, and sulphur only. Phosphorus, again, as usually known, is a nearly colourless, translucent, wax-like solid, which melts at a temperature only slightly above that of the hand, and which takes fire a few degrees higher; it is also extremely poisonous. Under special influences phosphorus can be made to assume the following properties:—A dark reddish-brown powder, resembling chocolate, which may be heated to 250° without taking fire, and which is non-poisonous. The substance is still phosphorus, and phosphorus only. This property possessed by certain of the elements of appearing in more than one form, of assuming, as it were, an *alias*, is called *allotropy;* the more uncommon form being spoken of as the *allotropic modification*, or the *allotrope* of the other.

From a study of the best known instances of this phenomenon, it is believed that allotropy, in all cases, is due to a difference in the number of atoms of the element that are contained in the molecule. In the case of ozone, which is the allotrope of oxygen, this is known to be the case. Ordinary oxygen molecules consist of two atoms, while the molecule of ozone is an aggregation of three oxygen atoms.

OZONE.

Molecular symbol, O_3. Molecular weight=48. Density=24.

History.—When an electrical machine is in operation a peculiar and characteristic smell is noticed in its vicinity. The same smell is sometimes observed in and about buildings, or other objects, when struck by lightning. In 1785 it was observed by Van Marum that when electric sparks were passed in oxygen, the oxygen acquired this peculiar smell. Schönbein (1840) showed that the oxygen obtained by the electrolysis of water also contained this substance having a smell, and he gave to it the name *ozone*, signifying *a smell.* Schönbein made a careful study of the substance, and found that it might be obtained by various other methods. The more recent work of Andrews, Soret, and Brodie has brought our knowledge of the constitution of ozone to its present state.

Occurrence.—Ozone is present in the atmosphere in extremely small quantities (see Atmospheric Ozone).

Modes of Formation.—(1.) Mixed with an excess of oxygen, ozone is best obtained by exposing pure dry oxygen to the influence of the silent electric discharge. This may be effected by means of the instrument shown in Fig. 36, known as "Siemens' ozone tube."

It consists of two concentric glass tubes, A and B. Tube A is coated upon its *inner* surface with tinfoil, which is brought into metallic contact with the binding screw D, as shown in the figure. Tube B is coated upon the *outer* surface, also with tinfoil, which is in metallic connection with binding screw C. These two surfaces of tinfoil are connected by means of their respective binding screws to the terminals of a Ruhmkorf coil, and the slow stream of oxygen which is admitted at E, and which passes along the annular space between the two tubes, is there exposed to the action of the silent electric discharge. A small portion of the oxygen so passing becomes converted into the allotropic modification, and the mixture of oxygen and ozone issues from the narrow tube at the opposite end of the apparatus.

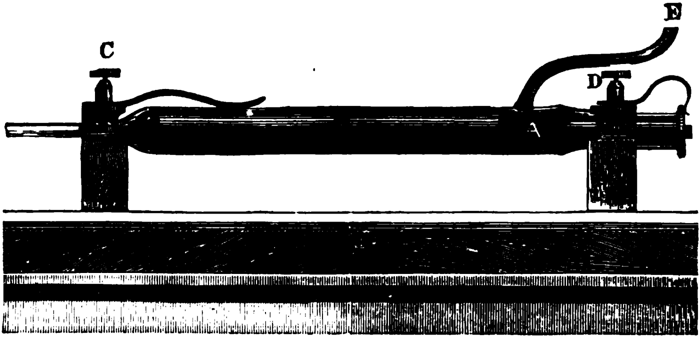

FIG. 36.

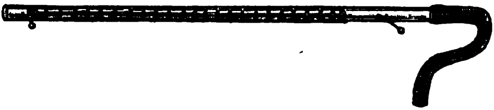

FIG. 37.

For general purposes of illustration, a very simple arrangement may be substituted for the above. It consists, as shown in Fig. 37, of a straight length of narrow glass tube having a piece of platinum wire down the inside, which passes out through the walls of the tube near to one end, and is there sealed to the glass. A second platinum wire is coiled round the outside of the tube, and these two wires are connected to the induction coil. On passing a slow stream of oxygen through the tube, the issuing gas will be found to be highly charged with ozone.

(2.) Ozone is also formed when an electric current is passed through water acidulated with sulphuric acid. Thus, in the ordinary electrolysis of water the oxygen evolved from the positive electrode is found to contain ozone in sufficient quantity to be readily detected, both by its odour and by other tests.

(3.) During many processes of slow oxidation at ordinary temperatures, ozone is formed in varying quantities. Thus, when phosphorus is exposed to the air an appreciable amount of ozone is formed. One or two short sticks of freshly scraped phosphorus are for this purpose put into a stoppered bottle containing air, and allowed to remain for a short time, when the air will be found to contain ozone.

(4.) Ozone is also formed during the combustion of ether upon the surface of red-hot platinum. When a spiral of platinum wire is warmed in a gas-flame, and while hot is suspended over a small quantity of ether contained in a beaker, the mixture of ether vapour and air undergoes combustion upon the surface of the platinum, which continues in an incandescent state so long as any ether remains. During this process of combustion a considerable quantity of ozone is formed. (See also Peroxide of Hydrogen.)

(5.) Ozone is formed during the liberation of oxygen in a number of the reactions by which that gas is obtained ; thus, from manganese dioxide and sulphuric acid the oxygen that is evolved contains sufficient ozone to answer to the ordinary test. In the same way, by the action of sulphuric acid upon barium peroxide or potassium permanganate, this allotrope is present with the ordinary oxygen that is evolved.

Properties.—As prepared by any of the methods described, ozone is always mixed with a large excess of unaltered oxygen, probably never less than about 80 per cent. of the latter gas being present. Even in this state of dilution it has a strong and rather unpleasant smell, which rapidly induces headache. When inhaled it irritates the mucous membranes, and is rather suggestive of dilute chlorine.

Ozone is a most powerful oxidising substance ; it attacks and rapidly destroys organic matter : on this account ozonised oxygen cannot be passed through the ordinary caoutchouc tubes, as these are immediately destroyed by it. It bleaches vegetable colours, and most metals are at once acted upon by it. Even metals like mercury, which are entirely unaltered by ordinary oxygen, are attacked by ozone. Its action upon mercury is so marked in its result, that the presence of exceedingly small traces of ozone can be detected by it ; the mercury is seen to lose its condition of perfect liquidity, and adheres to the surface of the glass vessel containing it, leaving "tails" upon the glass. Ozone converts lead sulphide (PbS) into lead sulphate ($PbSO_4$), and liberates iodine from potassium iodide—

$$2KI + H_2O + O_3 = O_2 + I_2 + 2KHO.$$

This property is generally made use of for detecting the presence of ozone, advantage being taken of the fact that iodine, when set free from combination in the presence of starch, gives rise to a deep blue-coloured compound, the reaction being one of extreme delicacy. In order to apply this test for ozone, strips of paper are dipped in an emulsion of starch to which a small quantity of potassium iodide has been added. These papers may be dried and preserved, and are usually spoken of as ozone test papers. When one of these papers is moistened with water, and placed in air containing ozone, the iodine is liberated from the potassium iodide, and being in the presence of starch, the paper instantly becomes blue by the formation of the coloured compound of starch. It will be obvious that this method of testing for ozone can only be relied upon when there is no other substance present which is able to decompose potassium iodide ; for example, when testing for ozone in the atmosphere, the presence of oxides of nitrogen or peroxide of hydrogen (both of which are capable of liberating iodine, and are liable to be present in the air) would materially vitiate the result (see also Atmospheric Ozone). The above decomposition of potassium iodide by ozone may be made use of as a test for ozone in another way, which, although less delicate, is also less likely to be vitiated by the presence of other substances. Blue litmus papers are dipped into water which has been rendered very feebly acid, and to which a small quantity of potassium iodide has been added. The papers may be dried and preserved. On moistening one of these papers with water and exposing it to ozone the iodide is decomposed as in the former case, and the potassium hydroxide which is formed, being a powerfully alkaline substance, converts the colour of the litmus from red to blue.

When heated to a temperature of about 250°, ozone is retransformed into ordinary oxygen; if, therefore, the ozonised gas obtained by means of the Siemens' ozone tube be passed through a glass tube heated by means of a Bunsen flame, the whole of the ozone will be decomposed, and the issuing gas will therefore be found to be without action upon the ozone test papers.

Ozone is also decomposed by certain metallic oxides, such as those of manganese, copper, and silver. The action appears to be one of alternate reduction and oxidation, the metallic oxide remaining unaltered at the conclusion, thus—

$$Ag_2O + O_3 = Ag_2 + 2O_2.$$
$$Ag_2 + O_3 = Ag_2O + O_2.$$

The oxidising power of ozone is due to the instability of the molecule and the readiness with which it loses an atom of oxygen, leaving a molecule of ordinary oxygen, thus—

$$O_3 = O + O_2.$$

The oxygen molecule is comparatively inert, but the liberated atom in its nascent state is endowed with great chemical activity. No change of volume accompanies these processes of oxidation by ozone, as the volume of the oxygen molecule (O_2) is the same as that of the ozone molecule (O_3), the third atom of oxygen being that which enters into new combination with the oxidised substance.

Ozone is soluble to a slight extent in water, imparting to the solution its own peculiar smell. 1000 c.c. of water dissolve about 4.5 c.c. of ozone.

Under the influence of extreme cold, ozone condenses to liquid having an intense blue colour. So deep is the colour, that a layer of it 2 mm. in thickness is opaque. This liquid is obtained by passing ozonised oxygen through a tube which is cooled by being immersed in boiling liquid oxygen, which has a temperature of −182.5°. At this temperature the ozone liquefies, but most of the oxygen with which it was mixed passes on. In a higher state of purity it has been more recently obtained by first liquefying ozonised oxygen, and then separating the more volatile oxygen by fractional distillation. Liquid ozone boils at −119°. It is described by Olszewski and Dewar as an extremely explosive substance.

Constitution of Ozone.—The fundamental difference between ordinary oxygen and its allotrope ozone lies in the fact that the molecule of the latter contains three atoms, while that of ordinary oxygen consists of only two. Ozone, therefore, is a polymer of oxygen ; its molecule is more condensed, three atoms occupying two unit volumes. This conclusion as to the constitution of ozone has been arrived at from the consideration of a number of experimental facts.

(1.) When oxygen is subjected to the action of the electric discharge, it is found to undergo a diminution in volume.* This was shown by Andrews and Tait by means of the tube seen in Fig. 38. The tube was filled with dry oxygen, which was prevented from escaping by means of the sulphuric acid contained in the bent portion of the narrow tube, which served as a manometer. When the silent discharge was passed through the oxygen, a contraction in the volume took place, indicated by a disturbance of the level of the acid in the syphon. When the tube was afterwards heated to about 300° C. and allowed to cool, the gas was found to have returned to its original volume, and to be devoid of ozone. This could be repeated indefinitely, the gas contracting when ozonised and re-expanding when the ozone was converted by heat into ordinary oxygen. As only a very small proportion of the oxygen was converted into ozone, this experiment alone afforded no clue as to the relation between the change of volume and the extent to which this conversion took place.

FIG. 38.

(2.) A small sealed glass bulb, containing a solution of potassium iodide, was placed in the tube before the experiment. The oxygen was ozonised, and the usual contraction noticed. The bulb was then broken, and on coming in contact with the ozone present the potassium iodide was decomposed, iodine being liberated. No further contraction, however, followed ; and, further, when the tube was subsequently heated to 300° and cooled, the gas suffered no increase in volume. By carefully estimating the amount of iodine that was liberated by the ozone, the actual amount of oxygen which had caused this liberation could be determined according to the equation—

$$2KI + H_2O + O = I_2 + 2KHO,$$

and it was found that the volume of oxygen so used up was exactly

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* "Chemical Lecture Experiments," new ed., Nos. 63, 64.

equal to the contraction which first resulted on the ozonisation of the oxygen.

These facts proved that when potassium iodide was oxidised by ozone a certain volume of ordinary oxygen was liberated, which was equal to the volume of ozone; and a certain volume was used up, which was equal to the original contraction.

These facts were explained by the supposition that ozone was represented by the molecular formula O_3; and its action upon potassium iodide may be expressed as follows—

$$2KI + H_2O + O_3 = O_2 + I_2 + 2KHO.$$

(3.) To prove the correctness of this supposition, however, it was necessary to learn the exact relation between these two volumes. This Soret did, by making use of the property possessed by turpentine (and other essential oils) of absorbing ozone without decomposing it; and he found that the diminution in volume which took place by absorbing ozone from ozonised oxygen was exactly twice as great as the increase in volume that resulted when the same volume of ozonised oxygen was heated.

This fact may be shown by means of the apparatus, Fig. 39.* The oxygen to be ozonised is contained in the annular space between the elongated hollow stopper, which reaches nearly to the bottom, and the outer tube. The turpentine is contained in a little sealed thin glass tube *d*, almost capillary in bore, which is held in position between four little projecting glass points *a* and *b* upon the stopper and outer tube. The temperature is main-

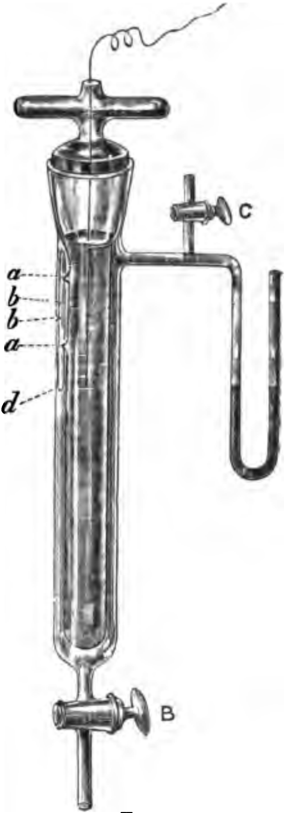

FIG. 39.

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* Newth, *Trans. Chem. Soc.*, 1896, p. 1298.

tained constant throughout the experiment by placing the apparatus in melting ice. One wire from the induction coil is dipped into the ice water, while the other passes into the dilute acid contained in the stopper. When the electric discharge is passed a portion of the oxygen is ozonised, resulting in a contraction in the volume which is indicated by a rise of the liquid in the gauge ; when sufficient contraction has taken place the discharge is interrupted, and the contents of the capillary tube brought into contact with the gas. This is done by a slight twist of the stopper, which thereby crushes the little tube and throws out the turpentine. Immediately a further contraction takes place, due to the absorption of the ozone by the reagent, and if the gauge be graduated it will be seen that this second contraction is twice as great as the first.

(4.) If the molecule of ozone be correctly represented by O_3, its density will be 24, as against 16 for oxygen ; and its rate of diffusion will be proportionately slower in accordance with the law of gaseous diffusion (see Diffusion of Gases, p. 84). Soret found that this was actually the case, and from his experiments the number 24 for the density of ozone receives conclusive confirmation.

CHAPTER III

COMPOUNDS OF HYDROGEN WITH OXYGEN

THERE are two oxides of hydrogen known, viz. :—

Hydrogen monoxide, or water	H_2O
Hydrogen dioxide	H_2O_2

WATER.

Formula, H_2O. Molecular weight = 18.02.

Until the time of Cavendish, water was considered to be an elementary substance. Priestley had noticed that when hydrogen and oxygen were mixed and inflamed, moisture was produced, and he had also observed that the water so obtained was sometimes acid. Cavendish showed that the water was actually the product of the chemical union of hydrogen with oxygen, and he also discovered that the acidity which this water sometimes possessed was due to the presence of small quantities of nitric acid; and he traced the formation of this acid to the accidental presence of nitrogen (from the atmosphere) with which the gases were sometimes contaminated.

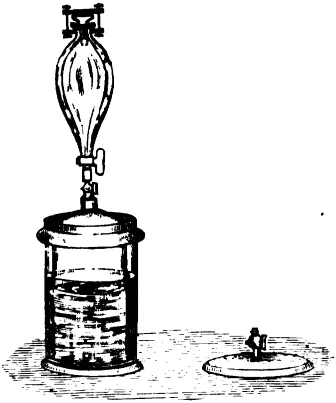

FIG. 40.

Cavendish filled a graduated bell-jar with a mixture of hydrogen and oxygen, in the proportion of two volumes of the former to one of oxygen, and he attached to the bell-jar a stout glass vessel resembling the pear-shaped apparatus shown in Fig. 40, which was perfectly dry and rendered vacuous. On opening the stop-cocks, gas entered the exhausted tube, which was furnished at the top with two platinum wires. The cocks were again closed and an electric spark passed through the mixed gases, thereby causing their explosion, when the interior surface of the previously dry glass vessel was found to be dimmed with a film of moisture. On again opening the stop-cocks more gas was drawn into the upper vessel, the same volume passing in as originally entered the evacuated apparatus. This showed that the two gases in their combination with each other had entirely disappeared. By repeatedly filling the vessel with the mixed gases and causing them to unite in this way, Cavendish succeeded in collecting sufficient of the water to identify the liquid, and prove that it was in reality pure water.

The more exact volumetric proportion in which oxygen and hydrogen combine to form water has been determined by modern eudiometric methods which have been developed from Cavendish's experiment. Accurately measured volumes of the two gases are introduced into a long graduated glass tube standing in the mercurial trough and provided with two platinum wires, by means of which an electric spark can be passed. The gases are caused to unite by means of the spark, and the contraction in volume is carefully observed. Fig. 41 shows the apparatus for this purpose. The long glass tube A having a millimetre scale graduated upon it, and having two platinum wires sealed into the glass near the upper and closed end, is completely filled with mercury and inverted in the trough of the same liquid : this tube is known as a eudiometer. A quantity of pure oxygen is then introduced into the tube, and the volume occupied by the gas carefully read off upon the graduations. Seeing that the volume occupied by a given mass of gas is dependent both upon the temperature and the pressure, each of these factors has to be taken into account in the process of this experiment. The temperature is ascertained by the attached thermometer T. The pressure under which the gas is, will be the atmospheric pressure at the time (ascertained by the barometer B placed near the apparatus) *minus* the pressure of a column of mercury, equal to the height of the mercury within the eudiometer above the level of that in the trough. This height is obtained in millimetres by carefully reading upon the graduated scale the level of the mercury in the trough and the top of the column in the tube, and the number of millimetres so obtained is deducted from the barometric reading. These observations are made by means of a telescope placed at such a convenient distance that the heat of the body may not introduce disturbances.

The data obtained give the volume of gas at a particular temperature, and under a pressure less than that of the atmosphere. By the process of calculation explained under the general properties of gases (p. 69), this is reduced to the standard temperature and pressure, viz., 0° and 760 mm.

A quantity of hydrogen is then introduced into the eudiometer, considerably in excess of that required for complete combination with the oxygen, and the volume again ascertained with the above precautions and corrections.

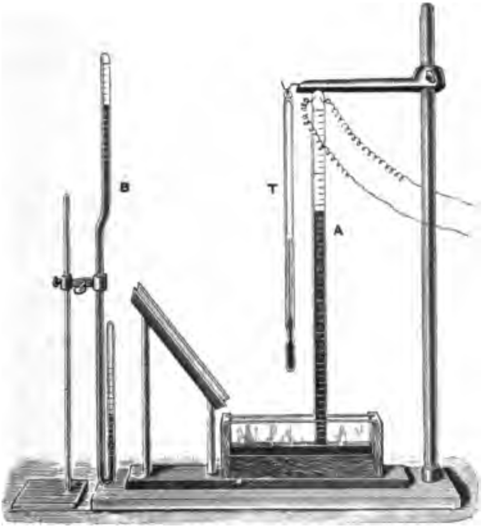

FIG. 41.

The difference between the first and second reading will give the volume of hydrogen which has been added.

The eudiometer is then firmly held down against a pad of caoutchouc upon the bottom of the trough, and the gases fired by an electric spark from a Ruhmkorff coil. A bright flash of light passes down the tube, and on releasing it from the indiarubber bed, mercury enters to fill the space previously occupied by the gases which have combined.

On allowing the instrument to once more acquire the temperature of the surrounding atmosphere, the residual volume is read off and corrected for temperature and pressure.

The following data have now been obtained :—

(1.) The volume of oxygen, corrected for temperature and pressure.
(2.) The volume of mixed oxygen and hydrogen, corrected for temperature and pressure.
(3.) The volume of residual hydrogen, corrected for temperature and pressure.

A concrete example will explain how the result is deduced from these observations :—

Corrected volume of oxygen used	45.35
Corrected volume after the addition of hydrogen . .	256.05
Corrected volume of residual hydrogen	120.10

256.05 − 45.35 = 210.70 = total volume of hydrogen employed.
210.70 − 120.10 = 90.60 = volume of hydrogen which has combined with 45.35 volumes of oxygen.

$$\therefore 45.35 : 1 :: 90.60 : 1.997.$$

∴ One volume of oxygen has combined with 1.997 volume of hydrogen to form water.*

The volume composition of water may be shown by analytical processes, as well as the synthetical method described above. This decomposition of water is most conveniently effected by means of an electric current. If the two terminals from a galvanic battery are connected to two pieces of platinum wire or foil, and these are dipped into acidulated water, bubbles of gas make their appearance upon each of the wires. If these two strips of platinum be so arranged in a bottle that all the gas evolved escapes by a delivery-tube (Fig. 42), it will be found that the gas explodes violently on the application to it

FIG. 42.

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* In accurate experiments the volume occupied by the minute quantity of water formed has to be taken into account, and a number of other corrections have to be made that are not mentioned in this outline description of the process.

of a lighted taper, showing it to be a mixture of oxygen and hydrogen. By modifying the apparatus in such a way that the gas from each platinum plate shall be collected in separate tubes, so arranged that the volumes of the gases can be measured, it is found that twice as much hydrogen is evolved, in a given time, as oxygen. A convenient form of voltameter is seen in Fig. 43, where the two measuring tubes are suspended over the platinum plates contained in a glass basin. The electrode, which is connected with the negative terminal of the battery, is the one from which the larger volume of gas, viz., the hydrogen, is evolved, while the oxygen is liberated at the positive plate.

When the volumes of the gases are carefully measured, it is found that they are not exactly in the proportion of two of hydrogen to one of oxygen, but that the oxygen is in deficit of this proportion. This is due, in the first place, to the greater solubility of oxygen in water than of hydrogen; and, secondly, to the formation of a certain quantity of ozone during the electrolysis, whereby there is a shrinking of volume in the proportion of three to two.

FIG. 43.

The "electrolysis of water," as this process is usually called, is not the simple phenomenon that at first sight it might appear to be. In the first place, pure water is not an electrolyte, and it is necessary either to acidulate it or to render it alkaline by the addition of sodium or potassium hydroxides. Solutions of these substances in water are electrolytes, and the substances are dissociated into their respective ions (see Electrolysis, Chap. xi.) to an extent depending upon the degree of dilution of the solution. In the case of water acidulated with sulphuric acid, these ions are in the main $2H^{\cdot}$ and SO_4''. (There are reasons for believing that to a limited extent, depending on concentration, the acid dissociates also into $H^{\cdot}$ and HSO_4'.) The first action of the electric current, therefore, is to cause these ions to travel to their respective electrodes and there to discharge their electricity. The hydrogen ions going to the cathode, and the SO_4'' ions to the anode. The hydrogen ions at the cathode, after becoming discharged of their positive electricity, unite to form molecules of hydrogen which then escape as gas. At the anode the SO_4''

ion, after discharging its negative electricity, undergoes chemical interaction with the water with which it is in contact, with the reformation of sulphuric acid and liberation of oxygen. The effect of the current may be represented thus—

At the Cathode.	At the Anode.
$2H_2$	$2SO_4 + 2H_2O = 2H_2SO_4 + O_2$.

Indirectly, therefore, the water is decomposed. As already stated, some of the nascent oxygen is converted into ozone, some also unites with water to form hydrogen peroxide, H_2O_2, and probably a still larger proportion of the deficit is due to the formation of persulphuric acid, which is always formed in solution at the anode. Berthelot considers that the variation of the proportion of hydrogen and oxygen evolved during the electrolysis of dilute sulphuric acid, from the proportion of two volumes of hydrogen to one volume of oxygen, is mainly, if not entirely, due to the formation of persulphuric acid.

It has been recently shown * that the purest "electrolytic gas," as this mixture of hydrogen and oxygen is called, is obtained by the electrolysis of pure barium hydroxide. Under these circumstances the oxygen contains no ozone or hydrogen peroxide.

The Volumetric Composition of Steam.—When a mixture of oxygen and hydrogen is exploded in a eudiometer, we have seen that a certain contraction of volume follows, due to the formation of water by the uniting gases. The oxygen and hydrogen that have entered into combination have disappeared as gases, the volume of the resultant water being practically negligible. It is important to know what relation exists between the volume of the uniting gases and the volume of the product of their combination when in a state of vapour—that is to say, what volume of steam is produced by the union of one volume of oxygen with two volumes of hydrogen; in other words, whether there is any molecular contraction in the formation of steam.

To ascertain this, the mixed gases, in the exact proportions to form water, must be made to combine under such circumstances that the product shall remain in a state of gas or vapour, so that its volume and that of the mixed gases may be measured under comparable conditions. For this purpose a mixture of oxygen and hydrogen, obtained by the electrolysis of acidulated water, is introduced into the closed limb of the U-shaped eudiometer shown in Fig. 44.† This tube is graduated into three equal divisions, indicated by the broad black bands, and is furnished with two platinum wires at the closed end. It is also surrounded by an outer tube, so that a stream of vapour from some liquid, boiling

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* Baker, *Jour. Chem. Soc.*, April 1902.

† See Experiments Nos. 74 and 75, "Chemical Lecture Experiments," new. ed.

above the boiling-point of water, can be made to circulate. The most convenient liquid for the purpose is amyl alcohol, which boils at 130°. In this way the eudiometer and the contained gases will be maintained at a constant temperature high enough to keep the water formed by their combination in the state of vapour.

The amyl alcohol is briskly boiled in the flask, and its vapour is led into the tube surrounding the eudiometer. The temperature of the mixed gases is thereby raised to 130°, and they occupy the three divisions of the tube when the mercury in the open limb is at the same level, that is, when the gases are under atmospheric pressure. The amyl alcohol vapour leaves the apparatus by the glass tube at the bottom, and is conveyed away and condensed. An electric spark is then passed through the gases by means of the induction coil. (In order to prevent the mercury from being forcibly ejected from the open limb of the U-tube at the moment of explosion, an additional quantity of mercury is poured in, and the open end is closed by the thumb when the spark is passed.) On bringing the enclosed gas again to the atmospheric pressure, by

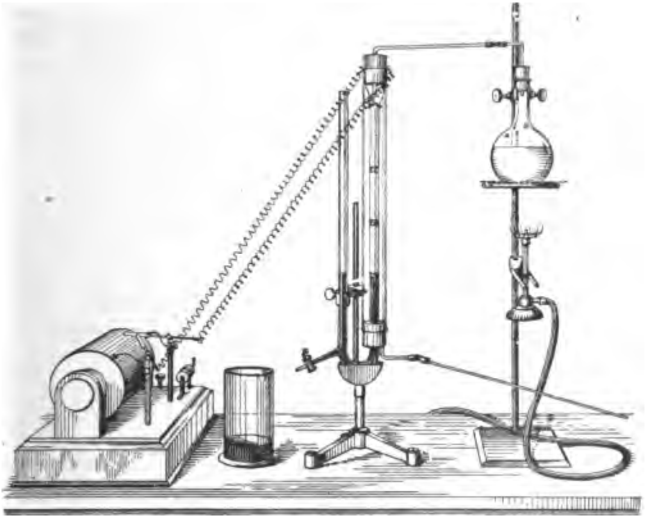

FIG. 44.

adjusting the level of the mercury until it is once more at the same height in each limb, it will be found that the mercury in the eudiometer is now standing at the second band; that is to say, the three volumes of gas originally present have now become two volumes of steam. This condensation is expressed in the molecular equation—

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

The Gravimetric Composition of Water.—Having learned the composition of water by volume, and knowing also that the relative weights of equal volumes of oxygen and hydrogen are as 15.88 : 1, the composition by weight can readily be calculated, thus—

$$\begin{array}{lr} \text{1 volume of oxygen} = & 15.88 \\ \text{2 volumes of hydrogen} = & 2.00 \\ \hline & 17.88 \end{array}$$

17.88 parts by weight of water are composed of 2.00 parts by weight of hydrogen and 15.88 parts of oxygen, or, expressed centesimally, we have—

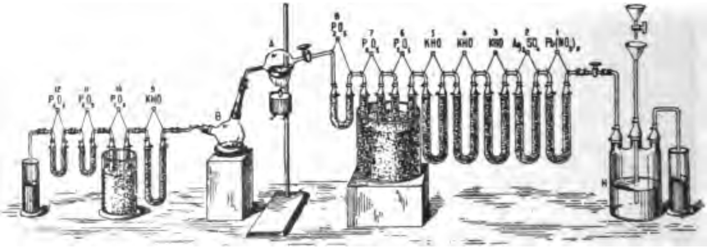

FIG. 45.

Oxygen	88.8
Hydrogen . . .	11.2
	100.0

The composition of water by weight has been experimentally determined with great care by a number of chemists.

The apparatus shown in Fig. 45 represents the method employed by Dumas (1843). When copper oxide is heated in a stream of hydrogen, the copper oxide is deprived of its oxygen, which unites with the hydrogen to form water—

$$CuO + H_2 = Cu + H_2O.$$

Dumas' method is based upon this reaction. A weighed quantity of perfectly dry copper oxide was heated in the bulb A, in a current of hydrogen generated from zinc and sulphuric acid in the bottle H, and rendered absolutely pure and dry by its passage through a series of tubes containing absorbents. The water formed by the union of the hydrogen with the oxygen of the copper oxide was collected in the second bulb, B, previously weighed; and the uncondensed aqueous vapour which was carried forward in the stream of hydrogen was arrested in the weighed tubes which follow. The increase in weight of the bulb B and the weighed tubes gave the total weight of water produced; while the loss of weight suffered by the copper oxide gave the weight of oxygen contained in that water. The difference between these two weights is the weight of the hydrogen that entered into combination with the oxygen.

As a mean of many experiments it was found that in the formation of 236.36 grammes of water the oxygen given up by the copper oxide was 210.06 grammes.

$$236.36 - 210.06 = 26.30,$$

therefore 236.36 grammes of water were made up of

$$\begin{array}{lr} \text{Hydrogen} = & 26.30 \\ \text{Oxygen} = & 210.06 \\ \hline & 236.36 \end{array}$$

The ratio of hydrogen to oxygen is therefore as 2 : 15.88.

Hydrogen prepared from zinc and sulphuric acid is liable to contain traces of

(1.) Hydrogen sulphide. This is absorbed in the first tube containing broken glass moistened with a solution of lead nitrate.

(2.) Arsenic hydride
(3.) Hydrogen phosphide
absorbed in the second tube, filled with glass moistened with silver sulphate.

(4.) Sulphur dioxide
(5.) Carbon dioxide
absorbed in the third tube, containing in one limb pumice moistened with a solution of potassium hydroxide, and in the other fragments of solid potassium hydroxide.

Tubes 4, 5, 6, and 7, containing solid potassium hydroxide and phosphorus pentoxide (the two latter being placed in a freezing-mixture), are for the purpose of withdrawing every trace of aqueous vapour. Tube 8 was weighed before and after the experiment in order to test the absolute dryness of the hydrogen that entered the bulb. In order to get rid of dissolved air, the dilute sulphuric acid used was previously boiled. Tubes 9, 10, 11 were weighed both before and after the experiment; while tube 12, which was not weighed, was placed at the end to prevent any absorption of atmospheric moisture by the weighed tubes.

Since the time of Dumas this subject has been reinvestigated by other experimenters, who have introduced various modifications into the process; thus, with a view to finding the weight of hydrogen directly and of eliminating many of the possible sources of error arising from the presence of impurities in the hydrogen, the hydrogen has been absorbed by palladium. The metal so charged with hydrogen can be weighed before and after the experiment, and the actual *weight* of hydrogen used directly ascertained.

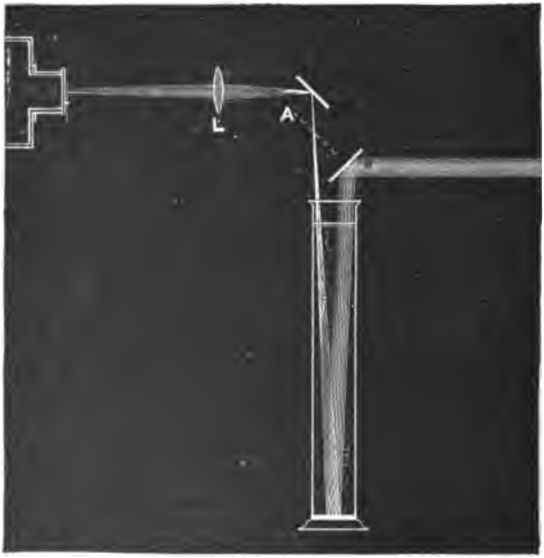

FIG. 46.

Most recently the matter has been investigated by Scott and Rayleigh, and the results obtained show only the slightest departure from the numbers obtained by Dumas.

Properties of Water.—Pure water is a tasteless and odourless liquid. When seen in moderate quantities it appears to be colourless, but when viewed through a stratum of considerable thickness it presents a beautiful greenish-blue colour. This colour may be seen by filling a horizontal tube about 15 feet long with the purest water, and passing a strong beam of light through it. It may also be perceived by directing a ray of light through a tall cylinder of water in the manner shown in the figure, and causing it to be reflected up through the water from the surface of a layer of mercury at the bottom; the immerging ray, being then reflected upon a screen, shows the characteristic colour of the water. By intercepting the ray by a hand mirror at A, the white light can be thrown upon the screen as a contrast to the greenish-blue tint.

Aitkin has recently shown that the presence of extremely finely divided suspended matters in water will give to the liquid the appearance of a blue colour. Thus, in tanks where water is being softened by the addition of milk of lime, after the bulk of the precipitated chalk has settled, and only the finest particles still remain suspended in the liquid, it is often noticed that the water appears to have a rich blue colour. The wonderful blue colour of the waters of many of the Swiss lakes is probably due in part to this optical phenomenon as well as to the intrinsic colour of the water. When a mass of pure snow, such as falls in high mountainous regions, is broken open in such a way that the light is reflected from side to side of the small crevice, the true greenish-blue colour of the water is very manifest.

Water is compressible to only a very slight extent; thus, under an additional pressure of one atmosphere, 1000 volumes of water become 999.95 volumes.

Small as this compressibility is, it exerts an important influence upon the distribution of land and water upon the earth. It has been calculated that owing to this compression, where the ocean has a depth of six miles, its surface is lower by 620 feet than it would be if water were absolutely non-compressible; and, calculated from the average depth of the sea, its average level is depressed 116 feet. The effect of this depression of the sea-level is that 2,000,000 square miles of land are now uncovered which would otherwise be submerged beneath the ocean.

Water is an extremely bad conductor of heat. A quantity of water contained in a tube held obliquely may be boiled by the application of heat to the upper layers without appreciably affecting the temperature of the water at the bottom; a fragment of weighted ice sunk to the bottom will remain for a long time unmelted, while the water a few inches above it is vigorously boiling. This low conductivity for heat is shared in common by all liquids that are not metallic. Indeed, Guthrie has shown, that water conducts heat better than any other substance which is liquid at the ordinary temperature, with the exception of mercury.

Steam.—Under a pressure of 760 mm., water boils at 100° (see p. 128), and is converted into a colourless and invisible gas or vapour. The visible effect that is observed when steam is allowed to issue into the atmosphere is due to the condensation of the steam in the form of minute drops of water. What is popularly called steam is in reality, therefore, not steam, but an aggregation of small particles of liquid water. The invisibility of steam is readily demonstrated by boiling a small quantity of water in a capacious flask; as the steam issues from the neck it condenses in contact with the cool air and presents the familiar appearance, but within the flask it will be perfectly transparent and invisible.

Ice.—At a temperature of 0° water solidifies to a transparent crystalline mass. In the act of solidification the water expands by nearly $\frac{1}{10}$th of its volume, 10 volumes of water become 10.908 volumes of ice: solid water, therefore, is specifically lighter than liquid water, and floats upon its surface. Water in this respect is anomalous, for in the case of most other substances the solid form is denser than the liquid. The disruptive force exerted by water at the moment of freezing is the cause of the bursting of pipes and other vessels containing water during winter; and it is also an important factor in the economy of nature in the disintegration of rocks and of soil. Under certain conditions water may be cooled many degrees below 0° without solidification taking place. Thus, if a small quantity of water contained in a vacuous tube be carefully cooled without being subjected to vibration, its temperature may be lowered to $-15°$ without it solidifying; a slight shock, however, at once causes it to pass into the solid state, when its temperature instantly rises to 0° (see p. 137). Although the exact temperature at which water freezes is liable to uncertainty from this cause, the point at which ice melts is, under ordinary circumstances, constant, viz., 0°. Under increased pressure ice will melt at temperatures below 0°; thus, Mousson found that, under a pressure of 13,000 atmospheres, ice melted at $-18°$. The melting-point of ice is lowered by about 0.0074° by each additional atmosphere of pressure (see p. 137).

Between the temperatures of $+4°$ and 100°, water follows the ordinary laws that govern the expansion and contraction of liquids due to change of temperature; if water be cooled from 100°, it gradually contracts until the temperature reaches 4°. Between this point and 0° it forms a remarkable exception to the general law, for, when cooled below 4°, it slowly expands instead of contracting, and continues expanding until 0° is reached, when it solidifies. At 4°, therefore, water expands whether it be heated or cooled; consequently, at this point it is denser than at any other temperature. This temperature is known as its point of maximum density. (The most accurate observations fix the exact point at 3.945°.)

The following table shows the change of volume suffered by water on being heated from 0° to 8° :—

1.000000	volumes at	0°	becomes
0.999915	”	+2°	”
0.999870	”	4°	”
0.999900	”	6°	”
1.000000	”	8°	

One cubic centimetre of water, measured at its point of maximum density and at 760 mm., is the unit of weight of the metrical system, and is called a *gramme.**

It is also at this temperature that water is taken as the unit for comparison of the densities of other liquids and of solids ; thus, when it is stated that the density or specific gravity of diamond is 3.5, it is meant that diamond is 3.5 times as heavy as an equal bulk of water measured at its point of maximum density.

The fact that water has a point of maximum density remote from its freezing-point is one of far-reaching consequences in the operations of nature.

When a mass of water, such as a lake, is exposed to the influence of a cold wind, the superficial layer of water is cooled, and thereby becoming specifically denser, it sinks to the bottom and exposes a fresh surface. This in its turn has its temperature lowered, and in like manner falls to the bottom. A circulation of the water in this way is set up until the entire mass reaches a temperature of 4°. At this point the further cooling of the surface-layer causes expansion instead of contraction, and the colder water becoming specifically lighter now floats upon the top, where it remains until it congeals. If water continued to contract as its temperature was reduced below 4°, the circulatory motion would continue until the whole body of the water was cooled to 0°, when solidification of the entire mass would take place. The reason that certain very deep

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* At the time this standard was first adopted, methods of measurement were less refined than at present. In reality the gramme is not *exactly* the weight of 1 c.c. of water at its point of maximum density.

waters seldom or never freeze is because the duration of the cold is not long enough to bring the temperature of the entire mass of the water down to 4°, and until that is effected no ice can form upon the surface.

The Solvent Power of Water.—Water is possessed of more general solvent powers than any other liquid ; that is to say, a larger number of substances are dissolved by water than by any other liquid. The solvent action of water upon gases, liquids, and solids, in so far as it is shared by other liquids, has been dealt with under the General Properties of Liquids (Part I., chap. xiii.).

Water of Crystallisation.—When solid substances are dissolved in water, and the water afterwards evaporated, the dissolved substance is frequently deposited in definite crystalline shapes. Many salts owe their crystalline nature to the fact that a certain number of molecules of water have solidified along with molecules of the salt, each molecule of the salt being associated with a definite number of molecules of solid water. The water molecules must be regarded as having entered into a feeble chemical union with the salt molecule, but a union which is of a somewhat different order from that which holds together the atoms of oxygen and hydrogen in the water molecules, or the atoms composing the salt in the salt molecule (see p. 66). Thus copper sulphate crystallises associated with five molecules of water, $CuSO_4,5H_2O$; magnesium sulphate with seven, $MgSO_4,7H_2O$. Water so associated with crystals is known as *water of crystallisation*, and the compound is called a *hydrate*.

Many salts are capable of crystallising with more than one definite number of molecules of water, depending upon the temperature at which the crystallisation takes place : thus sodium carbonate, crystallised at the ordinary temperature, has the composition $Na_2CO_3,10H_2O$; while at temperatures between 30° and 50° the salt that is deposited contains seven molecules of water, $Na_2CO_3,7H_2O$. Sodium chloride, crystallised from solution at $-7°$, has the composition, $NaCl,2H_2O$; while the crystals that are deposited at $-23°$ contain ten molecules of water, $NaCl,10H_2O$.

In such cases as these, the particular crystalline form of the salt differs with the different degrees of hydration.

Many crystalline salts, when exposed to the air, lose either some or all of their water of crystallisation, and in so doing lose their particular geometric form. Thus the salt, $Na_2CO_3,10H_2O$ (ordinary washing soda), when freely exposed, gradually loses its crystalline form and falls down to a soft white powder, which consists of small crystals of another form, having the composition Na_2CO_3,H_2O. This process is known as *efflorescence*, the crystals being said to *effloresce*. Other crystals undergo exactly the reverse change; they combine with moisture from the air, and pass into other crystalline forms containing more water of crystallisation, or in some cases they absorb sufficient moisture to cause them to liquefy. Such substances are said to *deliquesce*. This property of certain salts is made use of for withdrawing traces of water from either liquids or gases. Thus, such a liquid as ether may be freed from dissolved water by adding to it copper sulphate containing one molecule of water of crystallisation, $CuSO_4,H_2O$; this compound takes up water and passes into $CuSO_4,5H_2O$, and thereby has the effect of drying the ether. Gases in the same way are frequently dried by being passed through tubes containing calcium chloride from which the water of crystallisation has been removed. This substance absorbs water with avidity, passing into the hydrated salt $CaCl_2,6H_2O$.

The characteristic colours of certain salts are in many cases dependent upon the amount of water of crystallisation they contain. Thus cobalt chloride, $CoCl_2,6H_2O$, is a pink salt. If it be gently heated to 120° it loses its water and becomes $CoCl_2$, which has a rich blue colour. Solutions of this salt have been employed for the so-called *sympathetic inks*. The faint colour of the pink salt renders words written upon paper with its dilute solution practically invisible; but on warming the paper, and thereby expelling the water from the salt, the written characters appear in a blue colour, which again disappears as the salt is allowed to rehydrate itself by exposure to the air.

One of the most striking examples of this change of colour resulting from varying proportions of water of crystallisation is seen in the salt magnesium platino-cyanide, which crystallises under ordinary circumstances as a bright scarlet salt with seven molecules of water, $MgPt(CN)_4,7H_2O$. When this salt is heated to about 50° it loses two molecules of water, and is converted into a canary-yellow salt, $MgPt(CN)_4,5H_2O$. If the temperature be raised to 100° the yellow salt becomes white by the loss of three more molecules, the composition of the white salt being $MgPt(CN)_4,2H_2O$. When a solution of the salt is carefully evaporated to dryness in a dish and gently warmed, these colour changes will be rendered evident; and upon exposing the dried and white residue to the air, or by gently breathing into the dish, the salt rehydrates itself, and is converted into the crimson compound having seven molecules of water.

Many salts can have their combined water withdrawn by powerful dehydrating agents; thus, if a crystal of copper sulphate ("blue vitriol," $CuSO_4,5H_2O$) be immersed in strong sulphuric acid, the acid abstracts four out of the five molecules from the salt, leaving the nearly white salt $CuSO_4,H_2O$; or when alcohol is added to a solution of cobalt chloride, or to crystals of the salt, $CoCl_2,6H_2O$, the alcohol abstracts water, and the solution becomes blue.

When salts containing water of crystallisation are heated, it frequently happens that a portion of the water is more easily parted with than the remainder. Thus copper sulphate, $CuSO_4,5H_2O$, when heated to 100°, parts with four molecules of water, leaving the salt $CuSO_4,H_2O$; and in order to drive off this one remaining molecule, the temperature must be raised above 200°. Zinc sulphate (or white vitriol), $ZnSO_4,7H_2O$, in like manner loses six molecules of water at 100°, but retains the seventh until a temperature of 240° is reached. In order, therefore, to distinguish between the water that is more firmly held and that which is readily parted with, the term *water of constitution* is frequently applied to the former, and the fact is sometimes expressed in notation in the following manner:—

$$CuSO_4H_2O,4H_2O; \qquad ZnSO_4H_2O,6H_2O.$$

Natural Waters.—On account of the great solvent powers of water, this compound is never found upon the earth in a state of absolute purity; even rain, as it falls in regions far removed from the dirty atmosphere of towns, not only dissolves the gases of the atmosphere, but also small quantities of those suspended matters which are always present in the air. As soon as the rain reaches the earth, the water at once exerts its solvent action upon the mineral matter constituting the portion of the earth's crust over which it flows, and through which it percolates, and the liquid is rapidly rendered less and less pure as it travels on its course to lake or ocean.

Natural waters may be broadly divided into two classes, based upon the amount of dissolved impurities they contain. If the substances in solution are present in excessive quantities, or to such an extent as to be perceptible to the taste, the water is said to be a *mineral water;* while, on the other hand, waters that are not so rich in dissolved impurities are known as *fresh waters.*

Mineral Waters.—The most exaggerated examples of mineral waters are to be found in sea-water and in the waters of certain lakes, which, having no outlet, are fulfilling the purpose of enormous evaporating basins, in which the waters that flow into them are undergoing evaporation and therefore concentration; such, for example, as the salt lakes of Egypt, the Elton lake in Russia, and the Dead Sea. In waters of this description the total quantity of dissolved solid matter is very considerable, and, as in the case of the Dead Sea, is often deposited in crystalline masses round the shores of the lake. The following table gives the total amount of dissolved saline matter contained in 1000 grammes of certain of these waters:—

Irish Sea	33.86
Mediterranean Sea	40.0
Dead Sea	228.57
Elton Lake	271.43

As a typical example of a sea water, the composition of the water of the English Channel may be quoted; 1000 grammes of this water contain—

Sodium chloride	27.059	
Magnesium chloride	3.666	
Magnesium sulphate	2.296	
Calcium sulphate	1.406	
Potassium chloride	0.766	
Calcium carbonate	0.033	
Magnesium bromide	0.029	
		35.255
Water		964.745
		1000.000

Passing from these highly concentrated mineral waters, we find a large number of spring waters which are classed as *mineral*, not because the total quantity of foreign matter in solution is excessive, but rather because they contain an abnormally large proportion of a few special substances. Thus, large quantities of magnesium sulphate and chloride are found in such springs as those at Epsom and Friedrichshall. Others are found to contain considerable quantities of sodium sulphate and sodium carbonate; while those known as *chalybeate* waters contain ferrous carbonate in solution. Spring waters that are charged with unusual quantities of soluble gases are likewise placed in the category of mineral waters, such as the waters of Apollinaris and Seltzer, containing large quantities of carbon dioxide ; and the sulphur springs at Harrogate and Aachen, which hold in solution sulphuretted hydrogen as well as alkaline sulphides.

Fresh Waters.—The purest form of natural water is rain-water. The average weight of solid matter dissolved in rain-water, collected in the country and in perfectly clean vessels upon which it exerts no solvent action, is found to be 0.0295 part in 1000 parts of water. Collected in or near towns, rain-water always contains a larger amount of dissolved impurities, such as nitrates, sulphates, ammoniacal salts, and often considerable quantities of sulphuric acid : it is the acid nature of the rain that causes so much damage to stone buildings.

The nature and extent of the contamination that rain-water suffers after it has fallen must obviously depend very largely upon geographical and geological circumstances, and therefore there are no special features that are distinctly characteristic of waters from rivers, lakes, or springs.

Thus, the total solid impurity in 1000 parts of water from the river Dee at Aberdeen is 0.057, while that contained in the Thames is 0.30 parts.

The water of Loch Katrine only contains 0.032 part of solid matter dissolved in 1000 parts, while that of Elton lake contains as much as 271.43.

The same wide differences are also seen in spring waters from different geological strata. Spring waters from granite and gneiss rocks contain on an average 0.059 part of dissolved solid matter in 1000 parts, while those from magnesian limestone average as much as 0.665 part. As a broad general rule, river waters are found to contain less solid matter in solution than spring waters, and these in their turn less than deep well waters. Thus, comparing waters from different sources, and selecting only such samples as are known to be free from pollution from either sewage matter or other abnormal impurities, it will be seen that, with regard to the dissolved solid matter they contain, they fall in the following order :—

Total Solid Impurity Dissolved in 1000 *Parts of Unpolluted Waters.*

Rain-water (average of 39 samples)	.0295
Rivers and lakes (average of 195 samples)	.0967
Spring waters (average of 198 samples)	.2820
Deep well waters (average of 157 samples)	.4378

Hardness of Water.—Certain of the salts that are very frequently present as impurities in natural waters give to these waters the property that is known as *hardness.* The chief compounds that produce this effect are the salts of calcium and magnesium. The term *hardness* is applied to such waters on account of the difficulty of obtaining a lather, with soap, in the ordinary process of washing. Pure soap may be regarded as a mixture of the sodium salts of certain fatty acids (oleic, stearic, palmitic, &c.), which are soluble in pure water. In the presence of salts of calcium and magnesium the soap is decomposed, and an insoluble curdy precipitate is formed by the union of the fatty acid of the soap with the calcium and magnesium of the salts. Until the whole of the hardening salts have in this way been thrown out of solution, no lather can be obtained, and the soap is useless as a cleansing agent; but as soon as this point is reached, the addition of any further quantity of soap at once raises a lather on the water, and the soap is capable of acting as a detergent. This process of precipitating the salts of calcium and magnesium is known as *softening*, and in this instance the water is softened at the expense of the soap.

Hard waters often become less hard after being boiled for a short time, and this hardness which is so removed is termed the *temporary hardness.* The degree of hardness which the water still possesses after prolonged boiling is distinguished by the term *permanent hardness.* The diminution of the total hardness of a water by boiling is due to the fact that the soluble acid carbonates of calcium and magnesium are decomposed during this process into water, carbon dioxide (which escapes as gas), and the practically insoluble normal carbonates of these metals; thus, in the case of the calcium salt—

$$CaH_2(CO_3)_2 = H_2O + CO_2 + CaCO_3.$$

When such a water is boiled, the calcium carbonate is thrown down as a white precipitate, which gradually collects upon the bottom of the containing vessel. The "furring" of kettles, and the formation of calcareous deposits in boilers, is largely due to this cause.

In the case of waters that are highly charged with calcium carbonate, held in solution by dissolved carbonic acid, this deposition of calcium carbonate may even take place at the ordinary temperature, owing to the diffusion of the dissolved carbon dioxide into the air. It is in this way that those remarkable, and often beautifully fantastic formations, known as *stalactites*, have been produced in certain subterranean caves. Water charged with the soluble calcium carbonate, in slowly dropping from the roof of such a cave, loses a portion of its dissolved carbon dioxide, and, in consequence, deposits a certain amount of the calcium carbonate which was in solution. Each drop, as it slowly forms, adds its little share of calcium carbonate to the deposit, which thereby gradually grows, much as an icicle grows, as a dependent mass called a stalactite. Whether the water that drops from the stalactite has deposited the whole of its calcium carbonate, will depend largely upon the time occupied by each drop in gathering and dropping ; if, as often happens, the whole has not been precipitated, the remainder is deposited upon the floor of the cave, and a growing column of calcium carbonate, called a *stalagmite*, gradually rises from the ground until it ultimately meets the stalactite.

Clark's Process for Softening Water.—Waters whose hardness is due to the presence of the carbonates of calcium and magnesium can be deprived of their hardness by the addition to them of lime. The amount of hardness is first estimated, and such an amount of milk of lime is then added as is demanded by the following equation :—

$$CaH_2(CO_3)_2 + CaO = H_2O + 2CaCO_3.$$

In this way the soluble calcium salt is converted into the insoluble normal carbonate, which settles to the bottom of the tank.

The salts, which are mainly instrumental in causing the permanent hardness, are the sulphates of calcium and magnesium. The degree of hardness and its particular order, that is, whether temporary or permanent, will obviously be determined entirely by the particular geological formation from which the water is derived.

Potable Waters.—Undoubtedly the most important use to which water is put is its employment as an article of food to man, and since it has been proved beyond dispute that many virulent diseases, such as cholera, typhoid fever, and others, are propagated through the medium of drinking-water, it becomes a matter of the greatest sanitary importance that the waters supplied for this purpose should be as pure as possible. Excepting in very rare instances, where poisonous mineral matters accidentally gain access to drinking-water (as, for example, in the case of certain waters which are capable of attacking, and to a slight extent dissolving, the lead of the pipes through which they may be passed), the solid matters that are usually found in waters are not injurious to health. The living germs or bacilli, through whose agency zymotic diseases are caused, cannot be detected in a sample of water by any *direct* chemical analysis. A specimen of pure distilled water might be artificially contaminated with such organisms so as to constitute it a most virulent poison, and still chemical analysis would fail to detect the danger, and the water would be pronounced pure. Chemical analysis can, however, reveal the presence of excrementitious matter, and also of the characteristic products resulting from its decomposition: it can with certainty detect in the water the evidence of recent contamination with sewage matters, and it can also, with considerable precision, trace the evidences of its having been so contaminated at an earlier stage of its history. It cannot, however, distinguish between pollution with healthy and with infected excreta, and therefore it is necessary to regard with the greatest suspicion any water to which sewage has at any time gained access. Waters that are made use of for drinking purposes may be classified in the following order :—

Safe . .	1. Spring water.
	2. Deep well water.
	3. Mountain rivers and lakes.
Suspicious	4. Stored rain-water.
	5. Surface water from cultivated land.
Dangerous	6. River water to which sewage gains access.
	7. Shallow well water.

HYDROGEN PEROXIDE.

Formula, H_2O_2.

Occurrence.—This compound is occasionally found in small quantities in the atmosphere, and also in dew and rain.

Modes of Formation.—(1.) Hydrogen peroxide is produced in small quantities during the burning of hydrogen in the air. If a jet of burning hydrogen be caused to impinge upon the surface of water, the temperature of which is not allowed to rise above 20°, the water will be found, after a short time, to contain hydrogen peroxide.*

(2.) This compound is also produced by the decomposition of barium peroxide by carbonic acid. For this purpose a stream of carbon dioxide is passed through ice-cold water, into which from time to time small quantities of barium peroxide are stirred. Barium carbonate is precipitated, and a dilute aqueous solution of hydrogen peroxide is obtained—

$$BaO_2 + H_2CO_3 = BaCO_3 + H_2O_2.$$

(3.) Barium peroxide may be decomposed by either hydrochloric, sulphuric, silicofluoric, or phosphoric acid. Whichever acid be employed, the barium peroxide, previously mixed with a small quantity of water, is added gradually to the acid; which, in the case of either hydrochloric or sulphuric acid, should be diluted with from five to ten times its volume of water. The temperature of the mixture is not allowed to rise above 20°. Thus, in the case of hydrochloric acid—

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2,$$

the soluble barium chloride is removed by the addition of sulphuric acid, whereby barium sulphate is precipitated and hydrochloric acid formed—

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

The hydrochloric acid may be removed by adding a solution of silver sulphate, which precipitates silver chloride, leaving sulphuric acid in solution—

$$2HCl + Ag_2SO_4 = 2AgCl + H_2SO_4.$$

And, lastly, the free sulphuric acid is withdrawn by the addition of barium carbonate—

$$H_2SO_4 + BaCO_3 = BaSO_4 + H_2O + CO_2.$$

When sulphuric acid is employed for the decomposition of barium peroxide, the crystallised, or hydrated peroxide ($BaO_2,8H_2O$), is

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* See "Chemical Lecture Experiments," new ed., p. 74.

most advantageous for the purpose. This salt, made into a paste with water, is gradually added to the diluted and cooled acid, until the acid is nearly but not quite neutralised. The slight excess of acid is removed by the addition of the exact quantity of barium hydroxide (baryta-water) necessary to neutralise it, and the insoluble barium sulphate is removed by filtration. On a large scale silicofluoric acid or phosphoric acid is usually employed, preferably the latter, as it is found that small quantities of free phosphoric acid in hydrogen peroxide greatly retard its decomposition.

(4.) Hydrogen peroxide is also readily obtained by decomposing potassium peroxide by means of tartaric acid. The potassium peroxide is added to a cooled strong aqueous solution of tartaric acid, when potassium tartrate separates out, and an aqueous solution of hydrogen peroxide is obtained.

(5.) When small quantities of hydrogen peroxide are required for the purpose of illustrating its properties, it is most conveniently obtained by adding sodium peroxide to dilute and well-cooled hydrochloric acid, whereby sodium chloride and hydrogen peroxide are formed, both of which remain in solution—

$$Na_2O_2+2HCl=2NaCl+H_2O_2.$$

(6.) Hydrogen peroxide is formed in considerable quantity when ozone is passed through ether floating upon water. Probably a peroxidised compound of ether is first produced, which is then decomposed by the water. This production of hydrogen peroxide may readily be demonstrated by placing a small quantity of water and ether in a beaker, and suspending into the vapour a spiral of platinum wire which has been gently heated. The combustion of the ether vapour upon the wire, whereby the latter is maintained at a red heat, is attended with the formation of ozone, and this acting upon the ether, as already described, results in the production of hydrogen peroxide, which may be detected in solution in the water.

(7.) In small quantities, hydrogen peroxide is produced when moist ether is exposed to the action of oxygen, under the prolonged influence of sunlight.

Properties.—The dilute aqueous solution of hydrogen peroxide, obtained by the foregoing methods, is concentrated by evaporation over sulphuric acid in vacuo. In the pure condition it is a colourless and odourless, syrupy liquid, having an extremely bitter and metallic taste. The specific gravity of the liquid is 1.4532. The substance is extremely unstable, giving up some of its oxygen even at temperatures as low as −20°, and decomposing with explosive violence when heated to 100°. Hydrogen peroxide bleaches organic colours, but less rapidly than chlorine. When placed upon the skin it destroys the colour, and gives rise to an irritating blister. When diluted with water, and especially if rendered acid, the compound is far more stable, and in this condition may be preserved at the ordinary temperature for a considerable length of time. When such an aqueous solution is strongly cooled, it deposits ice, and in this way, by the removal of the frozen water, the solution may be concentrated. Hydrogen peroxide itself solidifies between −20° and −23°. When heated the solution is decomposed into water and oxygen—

$$H_2O_2 = H_2O + O.$$

Owing to the readiness with which hydrogen peroxide gives up the half of its oxygen and is converted into water, its properties are generally those of a powerful oxidising agent. It liberates iodine from potassium iodide; it converts sulphurous acid into sulphuric acid, and oxidises lead sulphide into lead sulphate. Its action upon lead sulphide is made use of in restoring something of the original brilliancy to oil paintings that have become discoloured. The "white-lead" used in oil paints is gradually converted into lead sulphide when such paintings are exposed to air, especially the air of towns, which is liable to contain small quantities of sulphuretted hydrogen. Lead sulphide being black, the picture slowly assumes a uniformly dark colour, until it is finally quite black. When such a discoloured picture is washed over with dilute hydrogen peroxide, the black sulphide is oxidised into the white lead sulphate—

$$PbS + 4H_2O_2 = 4H_2O + PbSO_4.$$

This compound is employed for bleaching articles that would suffer injury by the use of other bleaching agents, such as ivory, feathers, and even the teeth.

Hydrogen peroxide is also capable of oxidising hydrogen when that element in the nascent condition is brought in contact with this compound. Thus, if a dilute acidulated solution of hydrogen peroxide be subjected to electrolysis, oxygen will be evolved from the positive electrode, but no gas will be disengaged at the negative pole. The hydrogen, in the presence of the hydrogen peroxide, is oxidised into water—

$$H_2O_2 + 2H = 2H_2O.$$

Hydrogen peroxide, in many of its reactions, appears to act as a deoxidising agent; thus, manganese dioxide in contact with this substance is reduced to manganous oxide—

$$MnO_2 + H_2O_2 = MnO + O_2 + H_2O.$$

Similarly, silver oxide is reduced to metallic silver with the evolution of oxygen—

$$Ag_2O + H_2O_2 = Ag_2 + O_2 + H_2O.$$

In like manner, when ozone is acted upon by hydrogen peroxide, a reaction takes place exactly analogous to that with silver oxide, which will be the more obvious if the formula for ozone be written O_2O instead of O_3, thus—

$$O_2O + H_2O_2 = O_2 + O_2 + H_2O.$$

Although, in a sense, these reactions may be regarded as *reducing*, or *deoxidising*, actions, in essence they are not different from those which have been given as illustrative of the oxidising power of hydrogen peroxide. It will be seen that they all depend upon the readiness with which the compound parts with an atom of oxygen, but that in these latter cases the oxygen that is so given up is engaged in oxidising *another atom of oxygen*, contained in the other compound. Thus, in the case of silver oxide, its atom of oxygen is oxidised by the liberated oxygen from the hydrogen peroxide, and converted into the complete molecule of oxygen. By these reactions Brodie first demonstrated the dual, or diatomic, character of the molecule of oxygen.

When hydrogen peroxide is added to a dilute acidulated solution of potassium dichromate, a deep azure-blue solution is obtained (see Chromium), which affords a delicate test for this compound. To apply the test, the dilute hydrogen peroxide is shaken up with ether, and being soluble in this liquid, the ethereal layer which rises to the surface will contain nearly the whole of the peroxide; a few drops of acidulated potassium dichromate are then added, and the mixture again shaken, when the ethereal liquid will separate as a blue layer. In this way, the presence of

0.00025 grammes of hydrogen peroxide in 20 c.c. of water can be detected.

Hydrogen peroxide is decomposed by contact with many substances which themselves do not combine with the oxygen; thus charcoal, finely divided palladium, platinum, mercury, and notably silver, when brought into hydrogen peroxide, determine its decomposition into water and oxygen, the rapidity of the action being increased if the liquid be made alkaline. The action is doubtless catalytic, although in all cases the exact *modus operandi* is not clearly understood. In the case of silver it is believed that silver oxide (perhaps peroxide) is first formed, and then decomposed, thus—

$$Ag_2 + H_2O_2 = H_2O + Ag_2O$$
$$Ag_2O + H_2O_2 = H_2O + O_2 + Ag_2.$$

When hydrogen peroxide is added to solutions of the hydroxides of barium, strontium, or calcium, the peroxide of the metal is precipitated—

$$Ba(HO)_2 + H_2O_2 = 2H_2O + BaO_2.$$

The compound is deposited in crystals having the composition $BaO_2,8H_2O$.

With the hydroxides of the alkali metals, the peroxide (which is soluble in water) may be precipitated by the addition of alcohol; when in the case of sodium peroxide, crystals are obtained of $Na_2O_2,8H_2O$.

Hydrogen peroxide is a useful antiseptic; it possesses the advantages of being free from smell, without poisonous or injurious action upon the system, and of leaving as a residue, after having furnished its available oxygen, only water.

CHAPTER IV

NITROGEN

Symbol, N. Atomic weight = 14.04. Molecular weight = 28.08.

History.—Nitrogen was discovered by Rutherford in 1772. He showed that when an animal is placed in a confined volume of air for some time, and the air afterwards treated with caustic potash, to absorb from it the carbon dioxide ("fixed air"), there still remained a gas which was incapable of supporting either respiration or combustion. He called the gas *mephitic air.* Scheele was the first to recognise that this gas was a constituent of the air. Lavoisier applied the name *azote* to the gas, to denote its inability to support life. The name *nitrogen,* signifying the nitre-producer, was suggested by Chaptal, from the fact that the gas was a constituent of nitre.

Occurrence.—In the free state nitrogen is present in the atmosphere, of which it forms about four-fifths. Certain nebulæ have been shown by spectroscopic observation to contain nitrogen in the uncombined condition. In combination, nitrogen is found in ammonia, in nitre (potassium nitrate), and in a great number of animal and vegetable compounds.

Modes of Formation.—(1.) Nitrogen is very readily obtained from the atmosphere by the abstraction of the oxygen with which it is there mixed.* This is conveniently done by burning a piece of phosphorus in air, confined over water. The phosphorus in burning combines with the oxygen, forming dense white fumes of phosphorus pentoxide, which gradually dissolve in the water, and nitrogen remains in the vessel. The nitrogen obtained in this way is never quite pure, for the phosphorus becomes extinguished before the oxygen is entirely removed. It is also admixed with the other gases present in the atmosphere (argon, carbon dioxide, &c.; see Atmosphere), amounting in all to about 1 per cent. of the total.

(2.) Nitrogen in a purer state can be prepared from the atmos-

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* Experiments 254, 255, "Chemical Lecture Experiments," new ed.

phere by passing a stream of pure air over metallic copper contained in a combustion tube, and heated to redness in a furnace. The air is contained in a gas-holder, and is passed through two U-tubes, the first containing potassium hydroxide (caustic potash), in order to absorb the carbon dioxide; and the second filled with fragments of pumice moistened with sulphuric acid, in order to arrest the aqueous vapour. The purified air, on passing over the heated copper, is deprived of the whole of its oxygen, cupric oxide, CuO, being formed, while the nitrogen passes on and may be collected. This gas contains small quantities of argon (p. 256).

(3.) Oxygen is rapidly absorbed by a solution of cuprous chloride in hydrochloric acid; a ready method, therefore, of obtaining nitrogen from the air is to place a quantity of this solution in a stoppered bottle, and shake it up with the contained air. The colourless cuprous chloride solution quickly absorbs the oxygen, becoming dark in colour, and being converted into cupric chloride, the nitrogen of the air remaining in the bottle—

$$Cu_2Cl_2 + 2HCl + O = H_2O + 2CuCl_2.$$

(4.) Nitrogen is obtained by heating a strong solution of ammonium nitrite in a flask, the salt splitting up into water and nitrogen—

$$NH_4NO_2 = 2H_2O + N_2.$$

In practice it is found more convenient to employ a mixture of ammonium chloride and sodium nitrite—

$$NH_4Cl + NaNO_2 = NaCl + 2H_2O + N_2.$$

(5.) By heating a mixture of ammonium nitrate and ammonium chloride, a mixture of nitrogen and chlorine is evolved; the latter gas may be absorbed, by passing the mixture through either milk of lime or a solution of sodium hydroxide—

$$2NH_4NO_3 + NH_4Cl = 5N + Cl + 6H_2O.$$

(6.) Nitrogen is also evolved when ammonium chromate, or a mixture of potassium dichromate and ammonium chloride, is heated—

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2,$$

or—

$$K_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 + 2KCl + 4H_2O + N_2.$$

(7.) When ammonia is acted upon by chlorine it is decomposed, the chlorine combining with the hydrogen to form hydrochloric acid, and the nitrogen being liberated—

$$2NH_3+3Cl_2=6HCl+N_2.$$

If the chlorine be passed into a strong solution of ammonia, the hydrochloric acid which is produced combines with the excess of ammonia, forming ammonium chloride; thus—

$$8NH_3+3Cl_2=6NH_4Cl+N_2.$$

The chlorine, after being washed by passing through water, is bubbled through strong aqueous ammonia contained in a Woulf's bottle. As each bubble of chlorine enters into the ammonia, the combination is attended by a feeble yellowish flash of light, and a rapid stream of nitrogen is evolved. The nitrogen, which carries with it dense white fumes of ammonium chloride, should be scrubbed by being passed through a second bottle filled with fragments of broken glass moistened with water, and it can then be collected over water in the ordinary way, as shown in Fig. 47.* In preparing nitrogen by this reaction it is very necessary that the ammonia should be in considerable excess, otherwise there is liable to be formed the dangerously explosive compound of nitrogen and chlorine (see Nitrogen Trichloride).

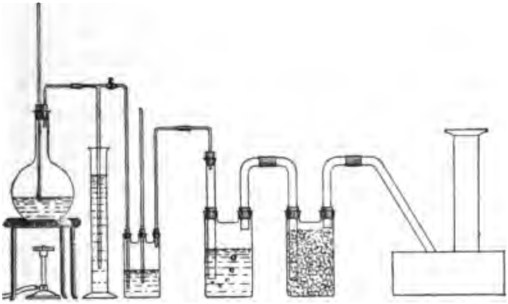

FIG. 47.

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* Experiment 261.

Properties.—Nitrogen is a colourless gas without taste or smell. It is slightly lighter than air, its specific gravity being 0.973 (air = 1). One litre of the gas at 0° C. and 760 mm. weighs 14 criths, or 1.250 grammes.

Nitrogen is only very slightly soluble in water, its coefficient of absorption at 0° C. being 0.020346.

Nitrogen will not burn, neither will it support the combustion of ordinary combustibles. It is not poisonous, but is incapable of supporting respiration.

Nitrogen is an extremely inert substance, combining directly, and with difficulty, with only a very few elements. Under the influence of the high temperature of the electric spark it can be made to unite directly with oxygen (see p. 235). Certain metals also combine directly with it, forming nitrides. Thus, when lithium or magnesium are heated in nitrogen, they form respectively NLi_3 and N_2Mg_3. This reaction may be conveniently shown by means of the apparatus seen in Fig. 48. A small quantity of powdered magnesium is placed in a hard glass tube, which is connected to a long narrow tube dipping into water, and a stream of nitrogen is passed through. When the air is all displaced the passage of the nitrogen is stopped and the magnesium strongly heated. At a red heat the nitrogen will be rapidly absorbed, and the water will be seen to rise in the long tube.

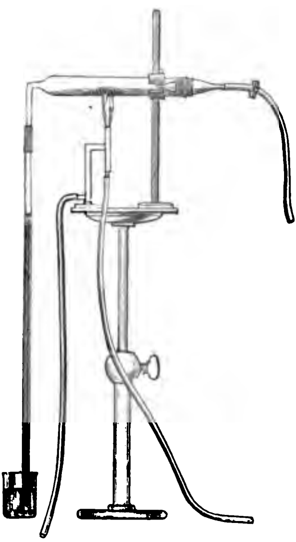

FIG. 48.

This property of nitrogen of uniting directly with magnesium was utilised in effecting the separation of the nitrogen of the air from the small quantities of argon and other "inert gases" contained in the atmosphere.

Although it is true that nitrogen in the elemental condition is an inert substance, the element itself is in reality possessed of strong chemical affinities. Indeed, the very inertness of its *molecules* may be regarded as an indication of the strong affinity between the two *atoms* which constitute the molecule. Nitrogen enters into the composition of an enormous number of compounds, and its atoms must be regarded as possessing great chemical activity. The formation of such compounds as the nitrides above mentioned may be quoted as an illustration. Although elementary nitrogen combines directly with comparatively few metals, and with most of these only at somewhat high temperatures, these compounds are readily produced if, instead of elementary nitrogen, nitrogen in combination with hydrogen (ammonia) be employed (see p. 278).

The critical temperature of nitrogen is − 149°, and when cooled to this point a pressure of 27.5 atmospheres causes its liquefaction. Under ordinary atmospheric pressure the liquid boils at − 195.5°; the gas, therefore, can be liquefied by the cold obtained by the rapid evaporation of liquid oxygen (see p. 78).

CHAPTER V

OXIDES AND OXY-ACIDS OF NITROGEN

NITROGEN combines with oxygen, forming five oxides :—

(1.)	Nitrous oxide (hyponitrous anhydride) .	N_2O.
(2.)	Nitric oxide	NO.
(3.)	Nitrogen trioxide (nitrous anhydride) .	N_2O_3.
(4.)	Nitrogen peroxide*	NO_2 and N_2O_4.
(5.)	Nitrogen pentoxide (nitric anhydride) .	N_2O_5.

Three oxy-acids of nitrogen are known, corresponding to the three oxides, Nos. 1, 3, 5 :—

Hyponitrous acid	HNO.
Nitrous acid	HNO_2.
Nitric acid	HNO_3.

The relation in which these three acids stand to their corresponding oxides may be seen by the following formulæ :—

Hyponitrous anhydride	$\left.\begin{matrix}N\\N\end{matrix}\right\}O.$	Hyponitrous acid	$\left.\begin{matrix}N\\H\end{matrix}\right\}O.$
Nitrous anhydride .	$\left.\begin{matrix}NO\\NO\end{matrix}\right\}O.$	Nitrous acid .	$\left.\begin{matrix}NO\\H\end{matrix}\right\}O.$
Nitric anhydride .	$\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O.$	Nitric acid .	$\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O.$

The most important of all these compounds, and the one from which all the others are directly or indirectly obtained, is nitric acid.

NITRIC ACID.

Formula, HNO_3. Molecular weight=63.05.

History.—Nitric acid, or *aquafortis*, was a well-known and valued liquid to the alchemists. Down to the time of Lavoisier

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* This name is usually applied to this substance both at low temperatures when its composition is expressed by the formula N_2O_4, and also at higher temperatures when the molecules have dissociated into the simpler molecules NO_2. In the strictest sense, however, they may be regarded as two oxides, and it has been suggested to name the one (N_2O_4) nitrogen tetroxide, and the other nitrogen peroxide.

(1776) its true nature was not known; he showed that oxygen was one of its constituents, but as to its other components he was uncertain. Its exact composition was determined by Cavendish.

Modes of Formation.—(1.) When an electric spark is passed through a detonating mixture of oxygen and hydrogen with which a certain quantity of air or nitrogen is mixed, the water that is produced by the union of the oxygen and hydrogen is found to contain nitric acid. This fact was first observed by Cavendish in the course of his investigations on the composition of water, when, owing to the accidental admixture of air with the mixed gases, oxygen and hydrogen, he found that the water resulting from the union was sometimes acid.

The direct union of nitrogen and oxygen may be brought about by allowing a series of electric sparks to pass between platinum wires in a confined volume of air, contained in a glass globe, as shown in Fig. 49. In a short time the air in the globe will become distinctly reddish in colour, owing to the formation of nitrogen peroxide. The rapidity of the formation of the red fumes will be greatly increased by compressing the air within the globe by means of a small compression pump, as indicated in the figure.

If a small quantity of water be introduced, and the contents of the globe shaken up, the red gas will be seen to dissolve in the water, which will then acquire an acid reaction, owing to the formation of nitric acid.

Similarly, when a jet of hydrogen is allowed to burn in air to which additional oxygen has been added, considerable quantities of nitrogen peroxide are formed. The hydrogen may be burnt from a jet, surrounded by a glass tube, as shown in Fig. 50, into which oxygen can be passed by means of the small bent tube at the bottom. On holding a clean dry cylinder over the flame, sufficient of the products of combustion will collect in a few seconds to show the presence of nitrogen peroxide.

This direct union of atmospheric oxygen and nitrogen has recently been made the basis of a manufacturing process. A stream of air is caused to pass through the electric arc at a rate sufficiently rapid to sweep away the products of the action and so prevent their dissociation. The nitrogen peroxide which is formed is condensed to the liquid state, and thereby separated from the other gases, by passing the mixture through a refrigerator.

(2.) Nitric acid is formed when nitrogenous animal matter undergoes slow oxidation in the air, in the presence of water and an alkali, the nitric acid combining with the alkali to form a nitrate. In this way nitrates are found in the soil, and from the soil often find their way into shallow well-waters of towns. In hot and rainless countries these nitrates are sometimes found as crystalline deposits on the surface of the soil, as in Chili and India (see Potassium Nitrate).

(3.) Nitric acid is prepared by acting upon potassium nitrate (*nitre-saltpetre*) with sulphuric acid. The nitre is placed in a glass retort, together with an equal weight of sulphuric acid, and the mixture gently heated. The nitric acid readily distils over, and may be collected in a cooled receiver. The residue in the retort consists of hydrogen potassium sulphate—

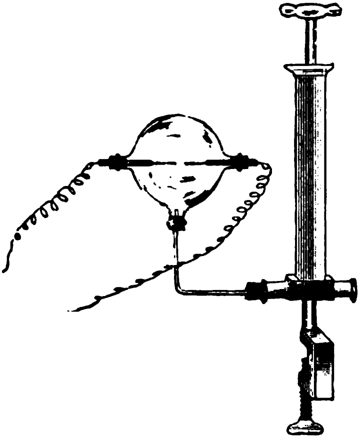

FIG. 49.

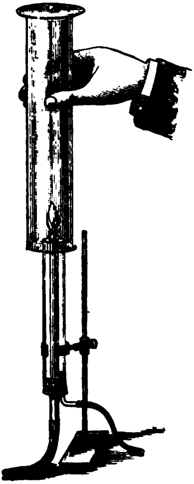

FIG. 50.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

The acid so obtained is not entirely free from water, and contains nitrogen peroxide in solution, which imparts to it a yellowish-red colour. To purify it, it is again distilled with an equal volume of sulphuric acid; and the redistilled acid is deprived of the last traces of dissolved peroxide of nitrogen, by causing a stream of dry air to bubble through it while slightly warm. Nitric acid so prepared may contain as much as 99.8 per cent. of anhydrous acid, HNO_3.

(4.) Nitric acid is an article of commercial manufacture. In this process potassium nitrate is replaced by the sodium salt, as being the cheaper material. The proportion of acid to sodium nitrate employed was formerly arranged in accordance with the equation—

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

It will be seen that the whole of the hydrogen of the sulphuric acid is thus replaced by the alkali metal derived from two molecules of the nitrate, and that two molecules of nitric acid result.

This reaction takes place in two stages; in the first we have—

$$(1) \quad NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

And then, as the temperature is raised, the hydrogen sodium sulphate reacts upon a second molecule of the nitrate, thus—

$$(2) \quad NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3.$$

The temperature necessary to effect this second stage, however, causes the decomposition of a certain quantity of the nitric acid—

$$2HNO_3 = H_2O + 2NO_2 + O.$$

And for this and other reasons, most modern manufacturers work only to equation No. 1.

The retorts usually employed for the manufacture of this acid are large cast-iron stills, which are sometimes lined, either entirely or in part, with fireclay, and which are built into a furnace in such a manner as to allow of their being heated as uniformly as possible. The charge of sodium nitrate (12 to 14 cwts.) and sulphuric acid is introduced, and the vapours carried off through an earthenware pipe (*c*, Fig. 51), connected to a series of earthenware pots, *b*, in the manner shown in the figure. The last of these jars is connected with a tower, filled with coke, down which water is caused to percolate, and any peroxide of nitrogen which escapes is thereby absorbed. The most modern form of still is not cylindrical, as shown in Fig. 51, but takes the shape of an enormous crucible with a dome-shaped lid; and is furnished with an exit pipe at the bottom, from which the liquid sodium bisulphate is run off.

Properties.—Nitric acid is a colourless liquid having a specific gravity of 1.53. It fumes strongly in the air, and has a peculiar and choking smell. It is extremely hygroscopic, absorbing moisture from the air with great readiness. Nitric acid is an intensely corrosive liquid: the strongest acid, when brought in contact with the skin, causes painful wounds, while in more dilute conditions it stains the skin and other organic materials a bright yellow colour. A quantity of strong nitric acid thrown upon sawdust causes it to burst into flame. When nitric acid is distilled it first

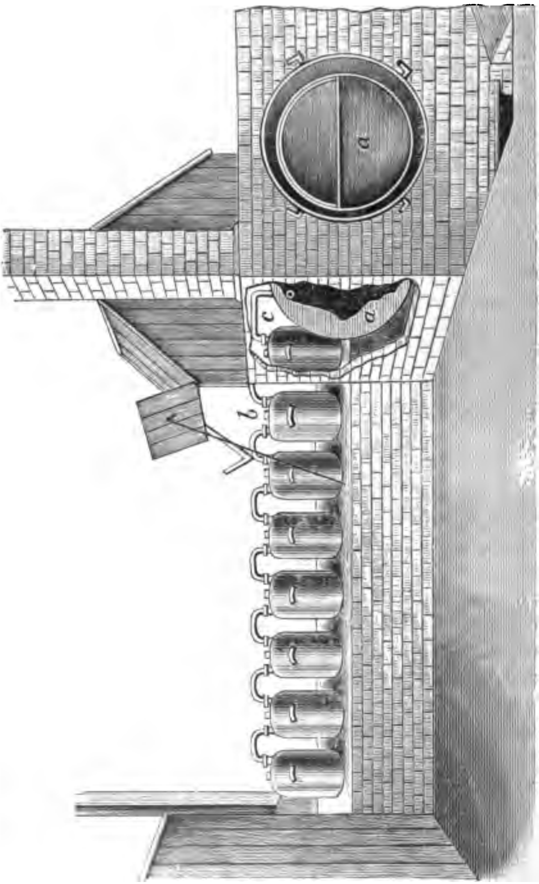

FIG. 51.

begins to boil at 86°, at the same time it is partially decomposed into water, nitrogen peroxide, and oxygen ; the distillate, therefore, gradually becomes weaker, and the boiling-point gradually rises. This continues until a certain point is reached, when both the temperature of the boiling liquid and the strength of the distillate remain constant. If, on the other hand, a weak acid be distilled, the distillate gradually increases in strength, until, when the same point is reached, the boiling liquid has again the same temperature.

This constant boiling-point is 120.5°, and the distillate which comes over at that temperature contains 68 per cent. of HNO_3. Whatever the strength of the acid, therefore, on being boiled it loses either nitric acid or water until the strength reaches 68 per cent., and this liquid boils at 120° C. The specific gravity of this acid at 15° is 1.414. It was formerly supposed that the acid of this strength constituted a definite hydrate, but Roscoe has shown that the strength of the acid is purely a function of the pressure, for by varying the pressure under which the distillation is conducted, acids of various compositions can be caused to distil at a constant temperature. Mixed liquids of this nature are known as *constant-boiling* mixtures, and are strictly analogous to constant-freezing mixtures (page 155).

When nitric acid is mixed with water there is a rise in temperature and a contraction in volume, the maximum effect being produced when the mixture is made in the proportion of three molecules of water with one molecule of acid.

Nitric acid is a powerful oxidising agent, on account of the readiness with which it parts with oxygen. Elements such as sulphur and phosphorus are oxidised into sulphuric and phosphoric acids ; arsenious oxide into arsenic acid ; and many protosalts are converted into persalts. It attacks a large number of metals, forming in many cases the nitrate. Its action upon metals is often of a complicated nature, and depends not only upon the particular metal, but also upon the strength of the acid, the temperature, and the presence of the saline products of the reaction ; thus, when nitric acid acts upon copper, the following reaction takes place—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

It is found, however, that as the amount of copper nitrate accumulates, the nitric oxide which is evolved is mixed more and more largely with nitrous oxide, N_2O, and even with nitrogen.

Again, when dilute nitric acid acts upon zinc, nitrous oxide is produced, according to the following equation—

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O.$$

When, however, strong nitric acid is employed, ammonia is formed, which combines with the excess of acid—

$$4Zn + 9HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_3.$$

In some cases, as with copper and silver, the presence of *nitrous* acid (either as an impurity in the nitric acid, or as a first product of its attack upon the metal) is believed to be a necessary condition of the action.

Owing to the strong oxidising properties of nitric acid, hydrogen is rarely isolated by the action of metals upon this acid, the hydrogen which is displaced from the acid being converted into water. With magnesium, however, free hydrogen is evolved.

The chief reactions of nitric acid may be broadly divided into three classes :—

(1.) With metallic oxides its behaviour is in common with other acids. It exchanges its hydrogen for an equivalent quantity of the metal, forming a nitrate, with the elimination of water, *e.g.*—

$$Ag_2O + 2HNO_3 = 2AgNO_3 + H_2O.$$

(2.) Reactions in which it acts as an oxidising agent ; as an example, its action upon iodine, which is converted into iodic acid, may be cited—

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

(3.) Actions in which hydrogen in an organic compound is replaced by the elements NO_2, with the elimination of H_2O, no gas being evolved. The conversion of cotton-wool, or cellulose, $C_{12}H_{20}O_{10}$, into gun-cotton, or nitro-cellulose, $C_{12}H_{14}O_{10}(NO_2)_6$, is an illustration of this class of reactions—

$$C_{12}H_{20}O_{10} + 6HNO_3 = 6H_2O + C_{12}H_{14}O_{10}(NO_2)_6.$$

Nitric acid is without action upon the so-called *noble* metals, gold and platinum.

Commercial nitric acid, which is of a reddish colour, is liable to contain many impurities : chlorine and iodic acid, derived from the Chili saltpetre ; iron, sulphuric acid, and sodium sulphate, carried mechanically over from the retorts ; and nitrogen peroxide, from the decomposition of the acid. From these it is purified by redistillation.

Nitric acid is a monobasic acid ; the salts of which, known as the nitrates, are for the most part readily soluble in water, and crystallise in well-defined forms. They are all decomposed at a high temperature, evolving oxygen and nitrogen peroxide, or oxygen and nitrogen, leaving an oxide of the metal.

The presence of a nitrate in solution is easily recognised by the following characteristic test. A solution of ferrous sulphate is first added to the solution containing the nitrate, and concentrated sulphuric acid is then cautiously poured down the side of the test-tube, held in a sloping position, so as to fall to the bottom without mixing with the solution. The sulphuric acid acting upon the nitrate liberates nitric acid ; this is reduced by the ferrous sulphate to nitric oxide, which, dissolving in the ferrous sulphate, forms a brown-coloured solution at the point where the two layers of liquid meet (see Nitric Oxide).

When nitric acid is added to hydrochloric acid, a mixture is obtained which is known by the name of aqua regia. This name was applied to it by the alchemists on account of its power of dissolving gold. Aqua regia is used in the laboratory for dissolving gold, platinum, and certain ores. Its solvent power depends upon the free chlorine which is evolved from the mixture—

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2.$$

NITROGEN PENTOXIDE (*Nitric Anhydride*).

Formula, N_2O_5. Molecular weight = 108.08.

Modes of Formation.—(1.) By withdrawing from nitric acid the elements of water, by means of phosphorus pentoxide—

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5.$$

For this purpose the strongest nitric acid is cautiously added to phosphorus pentoxide in a cooled retort, in the proportion demanded by the equation ; the mixture being made as far as possible without rise of temperature. The pasty mass is then gently heated, when the nitrogen pentoxide distils over, and, if collected in a well-cooled receiver, at once crystallises.

(2.) The method adopted by Deville, who discovered this compound (1849), was by passing dry chlorine over dry silver nitrate contained in a U-tube, which was kept at the desired temperature by being immersed in a water-bath. The following equation expresses the final result of the action—

$$2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O.$$

Properties.—Nitrogen pentoxide is a white solid substance, crystallising in brilliant prismatic crystals, which melt at 30° with partial decomposition. Between 45° and 50° it undergoes rapid decomposition, evolving brown fumes. It is a very unstable compound ; when suddenly heated it decomposes with explosive violence, and even at ordinary temperatures decomposition slowly takes place. It absorbs moisture rapidly, and when thrown into water it dissolves with the evolution of great heat—

$$N_2O_5 + H_2O = 2HNO_3.$$

When nitrogen pentoxide is gradually mixed with nitric acid, a compound is formed having the composition $2N_2O_5,H_2O$; which separates, on cooling, as a definite crystalline hydrate

NITROGEN PEROXIDE.

Formula, NO_2 and N_2O_4. Molecular weight = 46.04 and 92.08.
Density = 23.02 and 46.04.

Modes of Formation.—(1.) This compound may be prepared by mixing one volume of oxygen with two volumes of nitric oxide, and passing the red gas so obtained through a tube surrounded by a freezing-mixture—

$$2NO + O_2 = 2NO_2.$$

(2.) The nitrates of certain metals, when heated, are decomposed into nitrogen peroxide, oxygen, and an oxide of the metal ; thus, if dry lead nitrate be heated in a retort and the gaseous products of decomposition are conducted into a U-tube placed in a freezing-mixture, the nitrogen peroxide collects in the tube—

$$Pb(NO_3)_2 = PbO + N_2O_4 + O.$$

(3.) When arsenious oxide is gently warmed with nitric acid, a mixture of nitric oxide, NO, and peroxide, NO_2, is evolved, and if this gaseous mixture be passed through a cooled tube, it condenses to a blue liquid. On passing a stream of oxygen through this liquid it loses its blue colour, and is converted into a yellowish liquid which consists of nitrogen peroxide.

Properties.—At low temperatures nitrogen peroxide is a colourless crystalline compound. It melts at −9°, but requires a temperature as low as −30° to solidify it. At a temperature slightly above its melting-point the liquid begins to acquire a pale yellowish tint, which rapidly deepens until at the ordinary temperature it is a full orange colour. The liquid boils at 22°, and gives a vapour having a reddish-brown colour. The colour of the vapour also becomes deeper as its temperature is raised, until at 40° it is a dark chocolate brown, and almost opaque. On allowing the vapour to cool the reverse changes take place. This change of colour, as the temperature rises, is accompanied by a steady change in the density of the gas, as will be seen from the table :—

Temperature.	Density.	Percentage of NO_2 Molecules.
26.7°	38.3	20.00
60.2°	30.1	50.04
100.1°	24.3	79.23
135.0°	23.1	98.96
140.0°	23.02	100.00

The density required by the formula N_2O_4 is 46.04, while that demanded by the formula NO_2 is 23.02 ; hence as the temperature rises a process of dissociation goes on in which N_2O_4 molecules are broken down into molecules of the simpler composition. At 140° this process is complete, and the gas is entirely resolved into NO_2. It is believed that at low temperatures nitrogen peroxide has the composition represented by the formula N_2O_4, but that dissociation begins to take place even during the state of liquidity, as indicated by the gradual change of colour ; and therefore at temperatures between the boiling-point of the liquid, viz., 22°, and 140°, the gas consists of mixtures of molecules of NO_2 and N_2O_4. The calculated percentage of NO_2 molecules, which the gas contains at the temperatures at which the above densities are taken, are given in the third column.

Nitrogen peroxide is decomposed by water. At low temperatures, and with small quantities of water, nitric and nitrous acids are the products of the action, thus—

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

*

At the ordinary temperature, and with an excess of water, the following reaction takes place—

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

Gaseous nitrogen peroxide is incapable of supporting the combustion of a taper. Phosphorus, when strongly burning and plunged into the gas, continues its combustion with brilliancy, the temperature of the burning phosphorus being sufficiently high to effect the decomposition of the gas. Nitrogen peroxide is a suffocating and highly poisonous gas, and even when largely diluted with air rapidly produces headache and sickness.

Nitrogen peroxide unites directly with certain metals, giving rise to a remarkable series of compounds, to which the name nitro-metals, or metallic nitroxyls, may be given (Sabatier and Senderens).[*] Thus, when the vapour of nitrogen peroxide is passed over metallic copper (obtained by the reduction of copper oxide in a stream of hydrogen), the gas is rapidly absorbed by the metal with considerable rise of temperature, and a solid brown compound is formed. This substance is the copper-nitroxyl, and its composition is expressed by the formula Cu_2NO_2.

Copper-nitroxyl is a fairly stable compound, and is unacted upon by dry air. It is decomposed by water and by nitric acid, hence in its preparation care must be taken to free the nitrogen peroxide from these substances.

At a temperature of about 90° copper-nitroxyl is decomposed into copper and nitrogen peroxide. If, therefore, a quantity of the compound be sealed up in a bent glass tube, and the empty limb of the tube be immersed in a freezing-mixture while the compound is gently warmed, the nitrogen peroxide which is evolved will be condensed in the cold portion of the tube.

Similar compounds are formed with the metals cobalt, nickel, and iron.

Nitrous Acid, HNO_2.—This substance is not known in the pure state. Even in dilute aqueous solution it rapidly decomposes into nitric acid, nitric oxide, and water—

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The solution of this acid sometimes acts as a reducing agent, taking up oxygen from such highly oxidised compounds as permanganates or chromates and passing into nitric acid—

$$HNO_2 + O = HNO_3.$$

Under other conditions it exerts an oxidising action, as when it bleaches indigo, or liberates iodine from potassium iodide, being

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[*] *Bulletin de la Société Chimique*, September 1893.

itself reduced to nitric oxide and water, with the elimination of oxygen—

$$2HNO_2=2NO+H_2O+O.$$

The salts of nitrous acids, viz., the *nitrites*, are stable compounds. The nitrites of the alkalies are best prepared by carefully heating the nitrates; thus, when potassium nitrate is fused, it parts with oxygen and is transformed into potassium nitrite—

$$KNO_3=KNO_2+O.$$

At a higher temperature the nitrite is also decomposed.

Nitrites are decomposed by dilute acids evolving brown vapours, and in this way are at once distinguished from nitrates.

Nitrogen Trioxide.—There is considerable doubt as to the existence of this compound. It has been usually stated that it is formed by the action of nitric acid upon arsenious oxide, according to the equation—

$$As_4O_6+4HNO_3=2As_2O_5+2H_2O+2N_2O_3.$$

It has, however, been shown that the gas produced under these circumstances is not N_2O_3 but a mixture of molecules of NO and NO_2. It will be seen that a mixture containing equal volumes of these two gases will have a composition represented by the formula N_2O_3, therefore the above reaction may be regarded as taking place thus—

$$As_4O_6+4HNO_3=2As_2O_5+2H_2O+2NO+2NO_2.$$

Simultaneously with this reaction the following decomposition also goes forward—

$$As_4O_6+8HNO_3=2As_2O_5+4H_2O+8NO_2.$$

The result, therefore, of the action of nitric acid upon arsenious oxide is a mixture of nitric oxide and peroxide in varying proportions.

When this mixture is strongly cooled it condenses to a blue liquid, believed by some to be the true compound N_2O_3. Others regard it as merely a solution of the difficultly liquefied gas, NO, in liquid nitrogen peroxide, NO_2. If the two oxides are in a state of combination, it would appear to be at best a feeble union, for it has been shown that at temperatures as low as −90° the liquid slowly evolves NO, while at this temperature no nitrogen peroxide is given off.

The most recent work on the subject, however, based upon minute changes of volume which result when NO and NO_2 are mixed (Dixon and Peterkin, *Proc. Chem. Soc.*, June 1899), points to the conclusion that the reaction which may be expressed $N_2O_3=NO+NO_2$ is to a *slight* extent a reversible one; and that therefore a mixture of the two gases NO and NO_2 at ordinary temperatures actually does contain a *small percentage* of N_2O_3 molecules.

NITRIC OXIDE.

Formula, NO. Molecular weight = 30.04. Density = 15.02.

History.—Nitric oxide was first obtained by Van Helmont. Priestley, however, was the first to investigate this gas, which he termed *nitrous air*, and which was employed by him in his analysis of air.

Modes of Formation.—(1.) This gas is obtained by the action of nitric acid of specific gravity 1.2 upon copper or mercury. In practice copper is always employed.* The action may be represented thus—

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO.$$

The gas obtained by this method is always liable to contain nitrous oxide and even free nitrogen; the amount of these impurities rapidly increasing if the temperature be allowed to rise, and still more so as the amount of copper nitrate in solution increases.

(2.) Pure nitric oxide is readily obtained by the action of nitric acid upon ferrous sulphate. The reaction is best applied by generating the nitric acid from potassium nitrate and sulphuric acid in the presence of ferrous sulphate. A mixture of the two salts, in the proportion of about one part of nitre to four of ferrous sulphate, is introduced into a flask, with a small quantity of water. Strong sulphuric acid is dropped upon the mixture by means of a dropping funnel, and the mixture gently warmed, when a steady stream of pure nitric oxide is evolved—

$$2KNO_3+5H_2SO_4+6FeSO_4=2HKSO_4+3Fe_2(SO_4)_3+4H_2O+2NO.$$

A precisely similar result may be obtained by the reduction of potassium nitrate by means of ferrous chloride in the presence of hydrochloric acid, thus—

$$KNO_3+3FeCl_2+4HCl=3FeCl_3+KCl+2H_2O+NO.$$

Properties.—Nitric oxide is a colourless gas, having a specific gravity of 1.039. When brought into the air, it combines with the atmospheric oxygen, forming red-brown vapours, consisting of

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* Experiment 314, "Chemical Lecture Experiments," new ed.

nitrogen peroxide, the combination being attended with a rise of temperature. The formation of these red fumes in contact with oxygen is characteristic of this gas, thereby distinguishing it from all other gases. This property of nitric oxide renders it impossible to ascertain whether this gas has any smell, or is possessed of any toxicological action. Nitric oxide is only very sparingly soluble in water. It is the most stable of all the oxides of nitrogen, being able to stand a dull red heat without decomposition. It is not a supporter of combustion. A lighted taper, or a burning piece of sulphur, when introduced into the gas, are extinguished. If the temperature of the burning substance is sufficiently high to decompose the gas, combustion then continues at the expense of the liberated oxygen: thus, if a piece of phosphorus, which is freely burning in the air, be plunged into this gas, it continues its combustion with great brilliancy; if, however, the phosphorus be only feebly burning when thrust into the gas, it is at once extinguished. A mixture of carbon disulphide vapour and nitric oxide, obtained by allowing a few drops of the liquid to fall into a cylinder of the gas, burns, when inflamed, with an intensely vivid bluish flame, which is especially rich in the violet or *actinic* rays, and has on this account been sometimes employed by photographers to illuminate dark interiors. Nitric oxide is soluble in a solution of ferrous sulphate, forming a dark-brown solution, containing an unstable compound of ferrous sulphate and nitric oxide, $2FeSO_4,NO$. This compound is readily decomposed by heat, nitric oxide being evolved. By means of this reaction, nitric oxide may be separated from other gases. Nitric oxide is a difficultly liquefiable gas, its critical temperature being −93.5°: at this temperature a pressure of 71.2 atmospheres is required to liquefy it.

FIG. 52.

The composition of nitric oxide may be proved by heating a spiral of iron wire by means of an electric current in a measured volume of the gas (as shown in Fig. 52).* As the metal becomes red hot the gas is gradually decomposed and the oxygen combines

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* No. 321, "Chemical Lecture Experiments."

with the iron to form ferric oxide. The residual nitrogen will be found to occupy one-half the original volume.

Two vols. of nitric oxide, weighing 30.04
Contain 1 vol. of nitrogen, weighing 14.04

16.00 = weight of 1 vol. of oxygen.

Therefore we learn that two volumes of nitric oxide consist of one volume of nitrogen and one volume of oxygen united without condensation.

NITROUS OXIDE (*Hyponitrous anhydride, Laughing gas*).

Formula, N_2O. Molecular weight = 44.08. Density = 22.04.

History.—This gas was discovered by Priestley, and called by him *dephlogisticated nitrous air*.

Modes of Formation.—(1.) Nitrous oxide is formed by the reduction of nitric acid by certain metals, as zinc or copper, under special conditions (see Nitric Acid). These reactions, however, are never made use of for the preparation of the gas for experimental purposes.

(2.) The most convenient method for obtaining this compound is by the decomposition of ammonium nitrate. A quantity of the dry salt is gently heated in a flask fitted with a cork and delivery-tube. The salt rapidly melts and splits up into nitrous oxide and water—

$$NH_4NO_3 = 2H_2O + N_2O.$$

The heat should be carefully regulated, or the decomposition is liable to become violent, in which case nitric oxide is also evolved. Nitrous oxide being rather soluble in cold water, the gas should be collected either over mercury or over hot water.

When the gas is to be used for anæsthetic purposes, it should be purified by being passed first through a solution of ferrous sulphate to absorb any nitric oxide, and afterwards through caustic soda, to remove any chlorine which may have been derived from the presence of ammonium chloride in the nitrate.

Properties.—Nitrous oxide is a colourless gas, having a faint and not unpleasant smell, and a peculiar sweetish taste. Its specific gravity is 1.52. The gas is somewhat soluble in water, its coefficient of absorption at 0° being 1.3052. The solubility rapidly decreases as the temperature rises, as will be seen by the following table (Carius):—

1 c.c. Water at 760 mm. Dissolves	c.c. N_2O at 0° C. and 760 mm.
At 0°	1.3052
„ 10°	0.9196
„ 20°	0.6700
„ 25°	0.5962

The loss of gas during its collection over water in the pneumatic trough, arising from its solubility in that liquid, is therefore greatly lessened by using warm water. Nitrous oxide is much more readily decomposed than nitric oxide; a red-hot splint of wood is instantly rekindled, and bursts into flame when plunged into the gas. Phosphorus burns in it with a brilliancy scarcely perceptibly less dazzling than in pure oxygen. If a piece of sulphur which is only feebly burning be thrust into a jar of this gas, the sulphur is extinguished, the temperature of the flame not being sufficiently high to decompose the gas. When, however, the sulphur is allowed to get into active combustion before being placed in the gas, the combustion continues with greatly increased brilliancy. In all cases of combustion in nitrous oxide, the combustion is simply the union of the burning body with oxygen, the nitrogen being eliminated. From its behaviour towards combustibles, nitrous oxide might readily be mistaken for oxygen; it can, however, be easily distinguished from that gas by the fact that when added to nitric oxide it does not produce red vapours, whereas when oxygen is mixed with nitric oxide these coloured fumes are instantly formed.

When equal volumes of nitrous oxide and hydrogen are mixed in a eudiometer, and an electric spark passed through the mixture, the gases combine with explosion, water being produced and nitrogen set free; the volume of nitrogen so resulting being equal to that of the nitrous oxide employed. This compound, therefore, contains its own volume of nitrogen, and half its own volume of oxygen. Nitrous oxide, when inhaled, exerts a remarkable action upon the animal organism. This fact was first observed by Davy. If breathed for a short time, the gas induces a condition of hysterical excitement, often accompanied by boisterous laughter, hence the name laughing gas. If the inhalation be continued, this is followed by a condition of complete insensibility, and ultimately by death.

On account of the ease with which the state of insensibility can be brought about, this gas is extensively employed as an anæsthetic, especially in dentistry.

Nitrous oxide is a gas which is moderately easily liquefied ; at 0° C. a pressure of thirty atmospheres is required to effect its liquefaction.

Liquid nitrous oxide is colourless and mobile ; it boils at $-89.8°$, and when dropped upon the skin produces painful blisters. When thrown upon water, a quantity of the water is at once converted into ice ; mercury poured into a tube containing a small quantity of the liquid is instantly frozen. An ignited fragment of charcoal thrown upon the liquid floats upon the surface, at the same time burning with brilliancy. If the liquid be mixed with carbon disulphide, and placed in vacuo, the temperature falls to $-140°$. By strongly cooling the liquid, contained in a sealed tube, Faraday succeeded in solidifying it ; this may also be effected by the rapid evaporation of the liquid. The solid melts at $-102.7°$, and if placed upon the hand causes a painful blister ; in this respect it differs from solid carbon dioxide, which gasifies without previous liquefaction.

Hyponitrous Acid, NHO.—This substance has not yet been isolated, being only known in its salts and in aqueous solution.

When a solution of potassium nitrate, or nitrite, is acted upon by sodium amalgam (an alloy of sodium and mercury), the salt is reduced by the nascent hydrogen, evolved by the action of the amalgam upon water, and the potassium salt of hyponitrous acid is left in solution—

$$KNO_3+4H=2H_2O+KNO.$$

The solution, which is alkaline, owing to the presence of sodium hydroxide, is then made neutral by the addition of acetic acid, and silver nitrate added. A yellow precipitate is thrown down, consisting of silver hyponitrite, AgNO.

When a solution of potassium hyponitrite is acidified and then heated, the hyponitrous acid, which may be regarded as liberated by the acid, is broken up into nitrous oxide and water—

$$2HNO=N_2O+H_2O.$$

Nitrosyl Chloride,[*] NOCl.—This compound may be obtained by the direct combination of nitric oxide with chlorine—

$$2NO+Cl_2=2NOCl.$$

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[*] Tilden has shown that this is the only oxy-chloride of nitrogen that exists.

It is also formed by the action of phosphorus pentachloride upon potassium nitrite, thus—

$$PCl_5 + KNO_2 = NOCl + POCl_3 + KCl.$$

Nitrosyl chloride is formed together with chlorine when a mixture of nitric and hydrochloric acids is gently heated—

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

Nitrosyl chloride is also readily prepared by the action of nitrosyl hydrogen sulphate upon dry sodium chloride, thus—

$$(NO)HSO_4 + NaCl = NOCl + NaHSO_4.$$

Properties.—Nitrosyl chloride is an orange-yellow gas, which easily condenses when passed through a tube immersed in a freezing-mixture, to an orange-yellow liquid, which boils at about −8°. It is decomposed by water into nitrous acid and hydrochloric acid—

$$NOCl + H_2O = HNO_2 + HCl.$$

In a similar manner it is decomposed by metallic oxides and hydroxides, thus—

$$NOCl + 2KHO = KNO_2 + KCl + H_2O.$$

Nitrosyl chloride has no action upon gold and platinum, but it attacks mercury with the formation of mercurous chloride and the liberation of nitric oxide—

$$2NOCl + 2Hg = Hg_2Cl_2 + 2NO.$$

CHAPTER VI

THE ATMOSPHERE

THE atmosphere is the name applied to the gaseous mixture which envelops the earth, and which is commonly called the air. The older chemists used the word *air* much as in modern times the word *gas* is employed; thus they spoke of inflammable air, dephlogisticated air, alkaline air, and so on.

The air consists of a mixture of gases, the two chief ingredients being nitrogen and oxygen. Lavoisier was the first to clearly prove that oxygen was a constituent of the air, although Robert Boyle and others before him had shown that air was absorbed by metals in the process of forming a *calx*, and that the metal gained weight as the calx formed. When the fact that the air was composed of oxygen and nitrogen became established, various devices were adopted to determine the proportion of oxygen in it. Priestley's method was by means of nitric oxide. It depended upon the fact that when nitric oxide is mixed with air it combines with the oxygen, forming brown fumes which dissolve in the water. A contraction in volume therefore takes place, from which the volume of oxygen may be calculated. This method yielded results which seemed to show that there was considerable variation in the proportion of oxygen present in different samples of air, and the idea arose that the wholesomeness or goodness of the air was dependent upon the quantity of oxygen which it contained. Hence arose the term *eudiometry*, signifying *to measure the goodness.* Cavendish, on the other hand, as the result of a large number of experiments made by him, came to the conclusion that there was no difference in the samples of air that he experimented upon.

Since the time of Cavendish, eudiometric analysis has been brought to a state of great perfection and accuracy by Bunsen, Regnault, Frankland, and others. The conclusion to be drawn from the extended researches of these chemists is, that although the atmosphere certainly shows a remarkable uniformity of composition, there do exist perceptible, though very slight, variations in the amount of oxygen present at different places and at different times. Samples of air collected from all parts of the globe, from

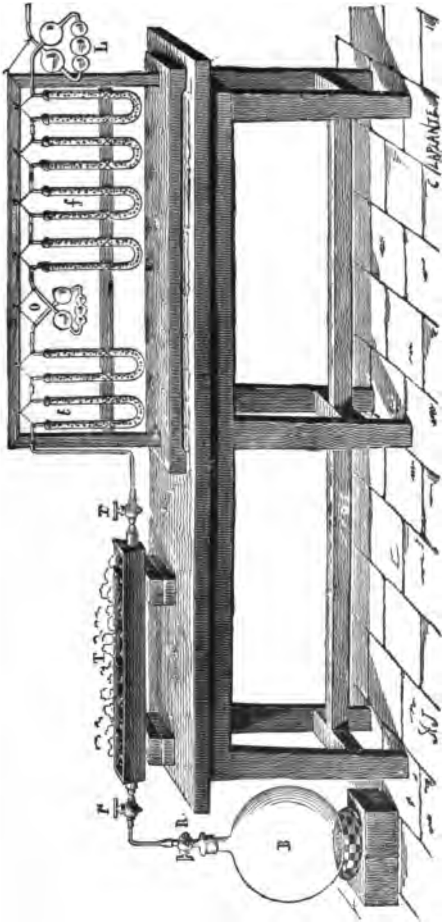

FIG. 53.

mid ocean, from high mountain peak, American prairie, and crowded cities, show a variation in the proportion of oxygen ranging from 20.99 to 20.86. Angus Smith has shown that in foggy weather the oxygen in the air in towns sometimes falls as low as 20.82. Samples of air taken from crowded theatres have been found to contain as little as 20.28, while in many mines the amount averages as low as 20.26.

The mean proportions of oxygen and nitrogen in the atmosphere may be given as—

Oxygen	20.96	parts by volume.
Nitrogen*	79.04	„ „
	100.00	

The composition of the atmosphere by weight was determined by Dumas and Boussingault (1841). In their method, air which was freed from carbon dioxide and moisture was slowly drawn through a glass tube containing a known weight of metallic copper, heated to redness. The oxygen combined with the copper, forming copper oxide, which was afterwards weighed, and the nitrogen passed into a vacuous flask, and was also weighed. The apparatus as employed by Dumas is seen in Fig. 53. B is a glass flask having a capacity of 10 to 15 litres, which was exhausted and then weighed. It was then attached, as shown, to the tube T, containing a known weight of metallic copper, and which was also exhausted. The bulbs L contained a solution of potassium hydroxide, and the tubes *f*, solid potash, for the removal of atmospheric carbon dioxide. The bulbs O contained strong sulphuric acid, and the tubes *t* were filled with pumice moistened with the same acid, by means of which the moisture was withdrawn from the air. When the copper was heated and the cocks partially opened, air, free from carbon dioxide and moisture, was slowly drawn over the heated metal, which was thereby converted into the oxide. At the conclusion of the experiment the globe and the tube T were reweighed. The nitrogen remaining in tube T was then pumped out and the tube once more weighed. The difference between the two last weighings of the tube, added to the gain in weight suffered by the globe, gave the nitrogen; while the difference between the original and final weights of the tube gave the increase of weight suffered by the copper, that is, the amount of oxygen. The result of numerous experiments gave the mean composition—

Oxygen	23	parts by weight.
Nitrogen *	77	„ „
	100	

---

* The small percentage of argon present is here included with the nitrogen.

A more modern method for estimating the amounts of oxygen and nitrogen in the air, based upon the same principle, namely, the absorption of the oxygen by heated metallic copper, is illustrated in Fig. 54 (known as Jolly's apparatus). The sample of air to be examined is allowed to enter the glass globe A (whose capacity is about 100 c.c., and which has been previously exhausted) by means of the three-way cock *b*. (The air is first dried, by being drawn through tubes filled with pumice moistened with sulphuric acid, on its way into the apparatus.) The bulb is then surrounded by the metal jacket B, which is filled with broken ice, and when the temperature has fallen to 0° the bulb is put into communication with the tube *d* by means of the three-way cock. The tube *g* is then raised or lowered, so as to bring the mercury in *d* to a fixed point in the tube at *m*, and the tension of the enclosed air is ascertained by the graduated scale behind tube *g*. The ice-jacket is then removed, and the spiral of copper wire within the bulb is heated to redness by the passage through it of an electric current. The

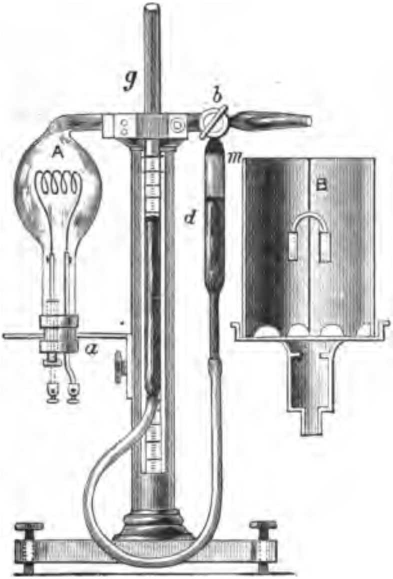

FIG. 54.

copper combines under these conditions with the oxygen, forming copper oxide, thereby reducing the volume of the contained gas. The globe is again cooled, and the tube *g* lowered to such a position that when communication is once more made between the globe and tube *d*, the mercury shall stand at the same point *m*.

From the observed tension of the gas before and after the experiment, the volume relations of the two constituents can be calculated. Thus, suppose the tension of the enclosed air to be 720.25 mm., and that of the residual nitrogen 569.28 mm., then for 1 volume of air the reduction would be—

$$\frac{569.28}{720.25}=.7904 \text{ vols.}$$

Therefore in 100 volumes the composition would be—

Nitrogen* = 79.04
Oxygen = 20.96

100.00

Besides oxygen and nitrogen, the air contains variable quantities of the following gases: aqueous vapour, carbon dioxide, argon, hydrogen, ammonia, ozone, nitric acid. With the exception of aqueous vapour, these substances are present only in relatively small proportions, and with some of them the amount is liable to considerable variation. Especially is this the case with the aqueous vapour, as the amount of this constituent present at any time is largely influenced by the temperature. The average composition of normal air may be taken as follows :—

	Vols. per 1000.
Nitrogen	769.5000
Oxygen	206.5940
Aqueous vapour	14.0000
Argon †	9.3700
Carbon dioxide	0.3360
Hydrogen	0.1900
Ammonia	0.0080
Ozone	0.0015
Nitric acid	0.0005
	1000.0000

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* The small percentage of argon present is here included with the nitrogen.

† The other four gases of the argon group taken together come to about 0.012 parts per 1000 (see page 270).

Aqueous Vapour.—For any given temperature there is a maximum amount of aqueous vapour which a given volume of air is capable of taking up : under these conditions the air is said to be *saturated with moisture* at the particular temperature. Thus 1 cubic metre of air is saturated with moisture at the various temperatures stated, when it has taken up the following weights of water :—

At 0°	4.871 grammes.	At 20°	17.157 grammes.
,, 10°	9.362 ,,	,, 30°	30.095 ,,

When air, saturated with moisture at say 20°, is cooled to 10°, the excess of water beyond 9.362 (the maximum for 10°) is deposited either as mist or rain. The temperature at which air thus begins to deposit moisture is called the *dew-point*. The deposition of moisture from the air caused by the lowering of the temperature is a matter of everyday observation. A glass vessel containing iced water becomes bedewed with moisture upon the outside as the air in its immediate vicinity is cooled. When a season of severe frost is suddenly followed by a warm wind, highly charged with aqueous vapour, it is not unusual to see condensed moisture collecting upon and streaming down the cold surface of walls. For the same reason, after the sun has set, and the heat from the ground has radiated, leaving the ground colder than the atmosphere, the temperature of the air is lowered, and it begins to deposit its aqueous vapour in the form of dew.

The amount of aqueous vapour in the air, or the humidity of the air, is estimated by meteorologists by means of an instrument called the wet and dry bulb thermometer.

Carbon Dioxide.—The proportion of this gas present in the air is also liable to considerable variation, although not through such a wide range as the aqueous vapour. The processes of respiration, combustion, and putrefaction are attended by the evolution of carbon dioxide, hence the amount of this gas present in closed inhabited places is greater than that in the open air ; in badly ventilated and crowded rooms the proportion sometimes rises to three parts in 1000 vols. Frankland has found that at high elevations the amount of carbon dioxide in the air is often, although not invariably, considerably above the normal.

At Chamounix (3000 feet) the amount of carbon dioxide was 0.63 per 1000 vols.
,, Grands Mulets (11,000 feet) ,, ,, ,, 1.11 ,, ,,
,, Mont Blanc (15,732 feet) ,, ,, ,, 0.61 ,, ,,

This fact is probably due to the absence, in these high regions, of the vegetation which is one of the chief natural causes operating to remove atmospheric carbonic dioxide (see Oxygen, page 188).

The amount of carbon dioxide is slightly higher during the night, and often rises considerably during foggy weather. Thorpe has shown that near the surface of the sea the amount of carbon dioxide in the air is slightly less, being on an average 0.300 volume per 1000.

Ammonia in the atmosphere is derived from the decomposition of nitrogenous organic matter. Although present in relatively very small quantities, it varies in amount very considerably. From the experiments of Angus Smith, 1000 grammes of air from various sources were found to contain the following amounts of ammonia:—

London . . .	0.05 gramme.
Glasgow . . .	0.06 „
Manchester. . .	0.10 „

The proportion of ammonia appears to be higher during the night than in the daytime, and immediately after heavy rain the amount is perceptibly diminished.

Rain-water always contains ammonia, although the amount varies greatly with changing atmospheric and climatic conditions. Lawes and Gilbert, Angus Smith, and others, have made a large number of estimations of the amount of ammonia in rain-water at various places and seasons, and under many different conditions.

Nitric Acid is produced in the atmosphere by the direct union of oxygen and nitrogen whenever a lightning flash passes through the air (see Nitric Acid). Rain which falls during or immediately after a thunderstorm is found to contain nitrates and nitrites.

These two nitrogenous compounds, ammonia and nitric acid, although present only in such small proportion in the atmosphere, fulfil a most important function in the economy of nature. From the experiments of Lawes and Gilbert, and others, it has been shown that most plants are unable to draw upon the free nitrogen of the atmosphere for the supply of that element which they require for the development of their structure and fruit.* Although they are surrounded by, and bathed in nitrogen, they cannot assimilate it. Plants that are growing in unmanured soil, therefore, derive their

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* Leguminous plants, such as clovers, vetches, beans, peas, which develop root-nodules or tubercles, are exceptions.

nitrogen from the ammonia and nitric acid which are present in the air, and which are washed into the ground by the rain. It has been found that a plant grown under such experimental conditions, as to exclude the possibility of its obtaining supplies of these nitrogenous compounds, will yield upon analysis exactly the same amount of nitrogen as was originally contained in the seed from which it grew.

Ozone.—The causes which operate in the formation of this substance in the air are at present imperfectly known; it is supposed that its occurrence is related to the development of electricity in the atmosphere. On account of the powerful oxidising character of ozone, its presence can never be detected in the air where much organic matter of an oxidisable nature is present, as is the case in the air of such places as malarial swamps, dwelling-houses, and large towns.

The amount of ozone in pure country air has been found to vary with the time of year, reaching a maximum in the spring-time, and gradually falling towards winter. Thorpe has found that in sea air the amount of ozone is practically constant during all seasons.

The usual method which is available for the detection and estimation of ozone in the air is extremely crude. It consists in exposing ozone test papers (see Ozone) to the air for a certain time, and comparing the colour that is produced with a standard scale of tints; moreover, other substances than ozone, which may be present in the atmosphere, will also liberate iodine from potassium iodide, and these are therefore measured as ozone. Besides the higher oxides of nitrogen, which, as we have seen, are formed in the atmosphere, and which liberate iodine from potassium iodide, it has been shown that peroxide of hydrogen is also present. The state of our knowledge at present, therefore, respecting the exact amount of atmospheric ozone and its variation is far from satisfactory; it is, indeed, quite possible that many of the effects which have been attributed to ozone are in reality due to peroxide of hydrogen. Thus it has been shown by Schönbein that this compound is formed during the evaporation of water, and this statement probably derives confirmation from the fact that its presence may be detected in rain-water. The salubrity of the air of the sea-shore, where large areas of wet sand and stones offer the most perfect conditions for the rapid evaporation of water, and consequently, for the formation of peroxide of hydrogen, may therefore be attributable as much to the presence of this substance as to the proverbial ozone.

Hydrogen.—The presence of this gas in sensible quantities as a constituent of normal air appears to have escaped notice until quite recently. When a quantity of liquefied air is subjected to fractional distillation, the first and most volatile portion which collects is found to be very rich in hydrogen.*

The elaborate researches of Gautier † show also that this hydrogen is not only present in the air of towns, but that it is a constituent of country air, air from high mountain regions, and of sea air; and he estimates the average proportion as about 2 volumes in 10,000 volumes of air, or roughly, about two-thirds that of the carbon dioxide. The chief sources of this hydrogen are indicated on page 171.

The various gases of which the air is composed are not combined, but are merely mingled together. The remarkable constancy of its composition, as regards the oxygen and nitrogen, led chemists at one time to suppose that these gases were in chemical union with each other in the atmosphere; but a number of facts which have since been learnt respecting these gases prove without doubt that this is not the case, and that the air is simply a mechanical mixture. This evidence may be briefly summed up as follows:—

(1.) When oxygen and nitrogen are mixed together in the proportion in which they occur in air, the resulting mixture behaves in all respects like ordinary air, and the mixing of the gases is not attended by any volumetric or thermal disturbance, such as would be expected to accompany the chemical union of two elements.

(2.) The degree to which air is capable of refracting light is found to be the mean of the refractive power of oxygen and nitrogen. Were these gases chemically combined, the compound should behave in this respect as other compound gases, where it is found that the refractive index is always either greater or less than the mean of that of the constituents.

(3.) According to a fundamental law of chemical science, the composition of a chemical compound is constant. Such a thing as variability in the composition of a compound is unknown. The proportion of oxygen and nitrogen, as we have seen, does vary in the air, although through only small limits, hence they cannot be united to form a compound.

(4.) The proportion by weight in which oxygen and nitrogen are

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* Dewar, *Nature*, December 20, 1900.

† Gautier, *Annales de Chimie et de Physique*, January 1901.

present in air bears no simple relation to the atomic weights of these elements.

(5.) When air is dissolved in water, the oxygen and nitrogen dissolve as from a simple mixture of these gases, in accordance to the law of partial pressures (see page 147).

(6.) The oxygen and nitrogen can be partially separated, by taking advantage of the different rates of diffusion of these two gases (see Diffusion of Gases, page 83).

The various gases of the atmosphere are maintained in a state of uniform admixture, in spite of their widely different densities, by the operation of two causes: first, air currents, which effect the rapid removal of large masses of air from place to place; and, second, their own molecular movements, which bring about the phenomena of gaseous diffusion.

Suspended Impurities in the Atmosphere.—Besides the gaseous constituents of the air, there is always present a certain quantity of suspended matter, both liquid and solid. The existence of this suspended matter in the air can be rendered evident from the fact that these minute particles are capable of reflecting light; if, therefore, a strong beam of light be passed through a darkened room, the track of the beam is distinctly visible, on account of its being reflected from innumerable particles floating about in the air, many of them appearing quite large. Pasteur has shown that this suspended matter can be removed by filtration through cotton wool.* Tyndall also has shown that in undisturbed air the suspended matter settles in the course of a few hours, leaving the air almost entirely free from this impurity. For this purpose the floor of a large oblong glass box was smeared over with glycerine. The box, after being hermetically closed, was then allowed to stand for twenty-four hours, during which time the suspended matter subsided and adhered to the glycerine. When a beam of light is allowed to pass through air that has been thus freed from suspended matter, there being nothing present to reflect the light, the beam cannot be seen; its track will be evident in the air of the room as it enters and leaves the box, but within the box it will be invisible (as represented in Fig. 55). To air in which a beam of light is in this way invisible, Tyndall has applied the term "optically pure."

The suspended matters are partly mineral and partly organic. Of the mineral matters, sodium chloride and certain sulphates

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* See Experiments 334 to 341, "Chemical Lecture Experiments," new ed.

are present in greatest quantity. These are thrown into the air in the sea-spray, and as the small globules of water evaporate they leave minute residual particles of saline matter, which, being driven by the wind, remain floating in the atmosphere. It is only very rarely, even at far inland places in Europe, that spectroscopic examination fails to detect the presence of sodium compounds in the air. In the air of islands, such as England, it is never absent. Sulphates are also produced by the oxidation and combustion of sulphuretted compounds; the amount of these, therefore, is greatly increased in the neighbourhood of towns.

The organic suspended matter of the air has of late years been made the subject of extended research. Pasteur has shown that amongst these organic substances are the germs and organisms which produce fermentation, putrefaction, and disease. Putrescible substances, such as milk, urine, flesh, &c., if themselves carefully freed from all such germs, may be preserved unchanged, for apparently any length of time, in air that has been deprived of all suspended matter. It is highly probable that the salubrity or otherwise of different places is associated with the nature and amount of the organic matter in the air, and it is certain that these organisms play a most important part in relation to the life and health of man. The feelings of lassitude and headache, which result from the prolonged breathing of the air of rooms containing many people, are brought about more by the poisonous effects of the organic emanations evolved during respiration than by any diminution in the supply of oxygen, or increase in the proportion of carbon dioxide in the air. The well-known and unpleasant smell that is perceived on first entering a crowded room is also due to the same cause, and it has been shown that the moisture which condenses from such an atmosphere upon a cold object, if

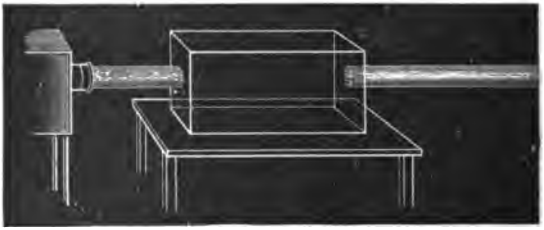

FIG. 55.

preserved for a short time, rapidly becomes putrescent, owing to the decomposition of this organic matter.

The presence of suspended matter in the air appears to exert a remarkable influence upon the formation and character of fogs. Aitkin has shown that those conditions which result in the formation of a fog in ordinary air are incapable of producing that effect in air that has been freed from suspended matter. It would appear that the suspended particles act as innumerable points, or nuclei, which facilitate the deposition of moisture, much in the same way as the crystallisation of a salt, from its solution, is known to start from any minute particles of foreign matter that may be floating in the liquid.

The height to which the atmosphere extends has been variously estimated. From observation of the flight of meteorites, it appears that even at a height of seventy to seventy-five miles the air still has a sensible degree of density. The air being elastic, and subject to the law of gravitation, its density, which is greatest at the earth's surface, rapidly diminishes as the altitude increases; thus, at about three and a half miles the density is only one-half, and at seven miles one-third, of that which obtains at the sea-level. From a consideration of the physical properties of gases, there is every reason to believe that in an extremely attenuated condition the atmosphere extends far into space, and it has been calculated that the pressure exerted by our atmosphere upon the surface of the moon is equal to about 1 mm. of mercury.

The density of the atmosphere varies at different points of the earth's surface, and at the same point at different times. The pressure exerted by the atmosphere is measured by the height of a column of mercury which it is capable of supporting, the instrument employed for the purpose being called the barometer. At the sea-level in the latitude of London, the average weight of the atmosphere is equal to that of a column of mercury 760 mm. at 0°, and this is taken as the *standard pressure of the atmosphere.*

THE ARGON GROUP OF ATMOSPHERIC GASES

History.—More than a hundred years ago Cavendish observed that when a mixture of nitrogen (*phlogisticated air*) and oxygen (*dephlogisticated air*) was confined in a glass tube over mercury along with a solution of caustic potash, and the gases exposed to the continued action of electric sparks, there was a small residue of gas (amounting to about $\frac{1}{120}$th of the volume of the nitrogen) which was not absorbed, and he raised the question as to whether the "phlogisticated air" of our atmosphere is entirely of one kind.*

This observation and speculation of Cavendish's remained buried until 1894, when Lord Rayleigh and Professor Ramsay announced to the world the discovery of a new gaseous constituent of the atmosphere.

In making exact determinations of the densities of gases, Lord Rayleigh found that nitrogen obtained from atmospheric sources always gave a slightly higher number than that obtained for nitrogen which was prepared from chemical compounds. On careful investigation, in conjunction with Professor Ramsay, it was found that this higher density of "atmospheric nitrogen" was due to the presence in the air of a hitherto unknown gas, which they succeeded in isolating, and to which they gave the name Argon (1894).

In the following year, in searching for probable sources of argon, Ramsay was led to examine the gas which was known to be occluded in certain minerals, notably in the rare minerals *clèveite* and *bröggerite*. This gas, which had hitherto been regarded as nitrogen, was found to give a spectrum the most characteristic line of which was a remarkably brilliant one in the yellow. The position of this yellow line proved to be coincident with the line D_3 of the solar spectrum, which is the characteristic line of a hitherto unknown solar element first observed by M. Janssen of Paris in 1868, the spectrum of which was studied by Frankland and Lockyer, who applied the name "helium" ("the sun") to the element. Subsequently Ramsay has shown that helium is present in the atmosphere, although in much smaller quantities than argon.

In the year 1898 the discoverer of argon announced to the Royal Society the discovery of two other gases which were associated with argon, to which he gave the names *neon* ("the new one") and *krypton* ("the hidden one"), and subsequently he discovered still another and denser gas, which has been called *xenon* ("the stranger"). The five gases, therefore, belonging to this group, in the order of their densities, are: helium, 2; neon, 10; argon, 19.95; krypton, 40.9; xenon, 64.0.

Not only are these five new gases elementary substances, but they possess many properties in common. They all are extremely

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* "Experiments on Air," *Phil. Trans.*, 75, 372, 1785.

inert elements, having apparently no chemical activities whatever. No compounds are known in which any one of them exists as a chemical constituent, and they have resisted all attempts to cause them to enter into chemical combination with any other element. Hence there is at present no *chemistry* of these strange substances. This being the case, the only light which can be thrown upon the complexity of the molecules of these elements is by the determination of the ratio of their specific heats at constant pressure and at constant volume, deduced from determinations of the wave-length of sound. This ratio is found to be 1.66, which is the same as that obtaining in the case of mercury vapour, the only other monatomic gas in which this ratio has been determined; whereas with diatomic gases, such as hydrogen, nitrogen, and oxygen, the ratio is 1.4.

ARGON.

Symbol, A. Density, 19.95. Atomic weight, 39.9.

Occurrence.—Argon is present in the atmosphere, where it exists to the extent of 0.937 per cent., or rather more than 1 per cent. of the "atmospheric nitrogen" is argon. It is also found in the occluded gases of certain specimens of meteoric iron, and in minute quantities in almost all natural waters, derived doubtless by solution from the atmosphere. Argon has not been met with in chemical combination with other elements, and no compounds containing this element are known.

Modes of Preparation.—(1.) Argon may be obtained from the atmosphere by sparking a mixture of air and oxygen. The nitrogen combines with the oxygen, and the oxidised product is absorbed by potash. When no further contraction of volume is obtained, the excess of oxygen is removed by alkaline pyrogallate, and the residual gas is the argon. Unless a high-tension alternating electric discharge is employed the process is extremely slow.

(2.) Argon may also be separated from the other atmospheric gases by first withdrawing the oxygen by means of red-hot copper, and after removing the carbon dioxide and aqueous vapour, passing the remaining gas over strongly heated magnesium turnings. The magnesium combines with the nitrogen (p. 232) and leaves the argon. In order to effect the complete absorption of every trace of nitrogen, the gas is passed backwards and forwards over the heated magnesium for many hours.

Recently it has been found that the metal calcium is a more efficient agent for the absorption of nitrogen. If, therefore, the "atmospheric nitrogen" be passed over a heated mixture of magnesium filings and pure dry lime the magnesium and lime interact, forming magnesia and calcium, which latter absorbs the nitrogen very rapidly and at a lower temperature than that required by metallic magnesium.

The purification of the argon thus obtained, and its complete separation from the other gases with which it is associated, was a problem which was only solved as a result of the later achievements by Dewar of obtaining liquid hydrogen in quantity. By means of the intense cold obtainable by liquid hydrogen, comparatively large quantities of argon were liquefied, and the liquid so obtained was then submitted to a process of fractional distillation. The liquid gases having the lowest boiling-points, namely helium and neon, are the first to evaporate, and by careful adjustment of the temperature of the refrigerating bath the denser gases, krypton and xenon, may be maintained even in the solidified state, while the whole of the argon in a state of practical purity can be distilled away.

Properties.—Argon is remarkable for its extraordinary inertness, a property which is indicated by its name, argon signifying "inactive." As already mentioned, it has hitherto resisted all attempts to cause it to unite chemically with any other element. The density of the gas is 19.95, and therefore its molecular weight is 39.9; and since argon is a monatomic element, its atomic weight and its molecular weight are the same.

Argon is about two and a half times as soluble in water as nitrogen, 100 volumes of water at 15° dissolving 4.1 volumes of argon. Owing to this superior solubility, the gases which are expelled from rain-water by boiling are slightly richer in argon than the original air before solution. The critical temperature of argon is − 117.4°, at which temperature the gas is liquefied by a pressure of about fifty-three atmospheres (or 40.20 metres of mercury). Liquid argon has a specific gravity of 1.212, and boils at − 186.1°. The boiling-point of argon, therefore, lies between those of the two chief constituents of the atmosphere, namely, oxygen and nitrogen, while its critical temperature is slightly above that of oxygen, as may be seen by the following comparison :—

	Boiling-point.	Critical Temperature.
Oxygen	− 182.5°	− 118.8°
Argon	− 186.1°	− 117.4°
Nitrogen	− 195.5°	− 149°

A very slight reduction of temperature below its boiling-point is sufficient to freeze argon to a white solid, the melting-point of which is – 187.9°; that is, less than two degrees below the boiling-point. The spectrum of argon is very complex. The most characteristic lines are two in the red (less refrangible than the red lines of either hydrogen or lithium), a bright yellow line (more refrangible than the sodium line), a group of bright green lines, and another group of strong lines in the violet. The general character of the spectrum depends upon the nature of the electric discharge employed. With an intermittent discharge the lines in the red and pale green are the most prominent, while with a Leyden-jar discharge the red and light green lines almost entirely disappear, giving place to lines in the dark green, blue, and violet.

HELIUM.

Symbol, He. Density, 2. Atomic weight, 4.

Occurrence.—The existence of this element in the universe may be said to have been first discovered by Janssen, who during a solar eclipse in 1868 observed a certain line in the yellow of the spectrum of the sun's chromosphere which was not coincident with that of any known terrestrial element. This unknown element was afterwards named *helium* by Frankland and Lockyer.

Terrestrial helium was discovered by Ramsay in 1895, in the gas which is contained in certain rare minerals, and which is evolved from them either when they are heated or when they are treated with dilute sulphuric acid. Chief among these minerals are clèveite, bröggerite, and uraninite, all of them minerals containing the metal uranium.*

Helium is present in minute quantities in the atmosphere, namely, to the extent of about 1 or 2 volumes in 1,000,000 volumes of air, as estimated by its discoverer.

Helium also occurs in certain natural waters, notably in the water from the Bath springs, which has been found to contain argon mixed with about 8 per cent. of its volume of helium.

Method of Preparation.—Helium is isolated from the atmosphere by a method consisting firstly of what may be described as *fractional liquefaction*, followed by fractional evaporation or distillation. When air is liquefied by the so-called self-cooling or recupe-

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* The amount of helium contained in 1 gramme of clèveite is about 3.2 c.c. (Ramsay), only about one half of which is given off by heat alone.

rative method in any of the modern air-liquefiers based upon Linde's original apparatus (see page 77), those portions of the air which escape liquefaction and pass out of the apparatus will obviously contain most of the constituents having the lowest boiling-points. Therefore, by collecting the gas which escapes from the air-liquefier under these circumstances, and compressing it into a vessel cooled by liquid air, a liquid is obtained which contains most of the more volatile constituents (namely, the helium and neon), with, of course, argon and some nitrogen. Thus, by this process of fractional liquefaction liquid air is divided into two fractions, one containing practically all the denser and least volatile constituents, namely, the krypton and xenon, the other containing the helium and neon.

The separation of the gases contained in the more volatile fraction is accomplished by fractional distillation or evaporation. At the low temperature obtainable by means of liquid hydrogen both argon and neon exert no vapour-pressure, being reduced to the state of non-volatile solids, and the helium in a state of purity can be pumped away from the mixture.

Properties.—Next to hydrogen, helium is the lightest known gas, its density being 2. Like all the other gases of this group its molecules are monatomic, its atomic and molecular weight therefore is 4. Helium is much less soluble in water than argon. The solubility of this gas in water forms an exception to the usual behaviour of gases, for it has been found that while its solubility diminishes with rise of temperature up to about 25°, between 25° and 50° the solubility slightly increases, as is shown by the following table.*

100 volumes of water at 760 mm. dissolve—

0°	10°	20°	30°	40°	50°
0.01500	0.01442	0.01386	0.01382	0.01387	0.01404 vols.

When induction sparks are passed through rarefied helium, the gas emits a brilliant yellow light with a tinge of apricot colour. When viewed through the spectroscope the most prominent and characteristic line is the intense yellow line D_3, which is accompanied by one bright red line, two in the green, and two in the blue. On reducing the pressure in the tube, the yellow light due to line D_3 gradually changes to a green, owing to the light from one of the green lines becoming greatly intensified.

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* Estreicher, "Z. Phys. Ch.," 31, 176.

Helium was first liquefied by Dewar (May 1898) by the use of boiling liquid hydrogen as a refrigerant; but the exact boiling-point of the liquefied helium has not yet been determined (1902), although it is believed to be not very far removed from that of hydrogen.

Like all the other gases of this group helium is chemically inactive.

NEON.

Symbol, Ne. Density=10. Atomic weight=20.

History.—From analogy with other natural families of elements and the numerical relations of the atomic weights of the different members, the discoverer of argon and helium was led to believe that another element should exist having an atomic weight between those of these two elements, and about sixteen units higher than that of helium. The long and careful search for this unknown element was at last rewarded by the discovery of neon, whose atomic weight was found to be 20, or exactly sixteen units above that of helium.

Although only present in minute quantities in the atmosphere, the discoverer estimates the amount as about ten times that of helium; that is to say, 1 or 2 parts of neon in 100,000 parts of air.

Neon is more readily liquefied than helium, but no exact determination of its boiling-point has yet been made.

The colour emitted by this gas when induction sparks are passed through it is a brilliant orange-pink. Its spectrum is characterised by a bright yellow line, D_5, and a great cluster of lines in the more orange part of the red end. It also exhibits other fainter lines throughout the spectrum.

KRYPTON AND XENON.

Krypton, symbol Kr. Density=40.9. Atomic weight= 81.8.
Xenon ,, X. ,, =64.0. ,, ,, =128.0.

These two denser gases are obtained by the fractional distillation of the heavier portion of liquid air obtained in the air-liquefier (see Helium). Large quantities of this liquid, amounting to 30 litres, were carefully evaporated, and the residual portion, after being entirely freed from nitrogen and oxygen, was again liquefied by means of liquid air. The constituents of this liquid were then separated by fractionation. As soon as most of the argon was removed, the residue consisting of krypton and xenon was easily solidified. Under these circumstances it was found that the krypton could be withdrawn by pumping, for at the temperature of liquid air solid krypton is appreciably volatile, while the solidified xenon is practically non-volatile. In the estimation of the discoverer, air contains only about one part of krypton in one million parts; while of xenon the proportion is about one part in twenty millions. The boiling and melting points of krypton are −151.7° and −169° respectively, while those of xenon were found to be −109.1° and −140°.

The light emitted by krypton, under the influence of the induction spark, is a yellowish-green colour, while that given by xenon under the same circumstances is more of a sky-blue.

The most prominent lines in the spectrum of krypton are two very near together in the red, one bright yellow line and one strong green line; besides which there are a few in the blue and violet. The brilliant green line (wave length, 5570.5) has attracted special notice, as it is considered highly probable that this line may prove to be coincident with the chief line in the aurora spectrum.

The spectrum of xenon, like that of argon, is markedly different as the electric discharge is modified. With the intermittent discharge the prominent lines are four in the red end, and a number of strong lines in the blue and greenish-blue. With the "jar" discharge the red and blue lines become very reduced or altogether disappear, and their place is taken by a number of lines in the bright green.

The relative proportion in which these gases are believed to be present in the atmosphere has been estimated provisionally by the discoverer as follows:—

Helium,	1 to 2	parts	per	1,000,000	of air.
Neon,	„	„	„	100,000	„
Argon,	0.937	part	„	100	„
Krypton,	1	„	„	1,000,000	„
Xenon,	1	„	„	20,000,000	„

Or, expressed in parts per 1000, to compare more readily with the figures in the table on page 256:—

Argon	9.37
Neon	0.01
Helium	0.001
Krypton	0.001
Xenon	0.00005

The following table (Ramsay) gives the latest physical constants for the members of this strange group of new elements.

	Density.	Atomic Weight.	Boiling-Point.	Melting-Point.	Critical Temp.	Critical Pressure.
Helium .	2	4	...	...	...	...
Neon . .	10	20	...	...	...	...
Argon . .	19.95	39.9	− 186.1°	− 187.9°	− 117.4°	52.9 Ats.
Krypton .	40.9	81.8	− 151.7°	− 169°	− 62.5°	54.2 ,,
Xenon . .	64.0	128.0	− 109.1°	− 140°	+ 14.75°	57.2 ,,

The members of this group, while exhibiting many close resemblances, such as the monatomic nature of their molecules, their remarkable inertness, &c., show also that gradation of properties which is met with in other natural groups of elements. This appears by the results tabulated above, as well as by such other properties as the refractive indices, atomic volumes. &c.

CHAPTER VII

COMPOUNDS OF NITROGEN AND HYDROGEN

FOUR compounds of nitrogen with hydrogen have been prepared, namely:—

Ammonia	NH_3.
Hydrazine	N_2H_4 or $(NH_2)_2$.
Hydrazoic acid	N_3H or HN_3.
Ammonium hydrazoate . .	N_4H_4 or NH_4N_3.

AMMONIA.

Formula, NH_3. Molecular weight = 17.04. Density = 8.52.

History.—Ammonium salts, and also the aqueous solution of ammonia, were known to the alchemists. It was termed by Glauber, *spiritus volatilis salis armoniaci*, being obtained by the action of an alkali upon *sal-armoniacum*. Subsequently the name *spirits of hartshorn* was applied to the ammoniacal liquid obtained by the destructive distillation of such refuse as hoofs and horns of animals. The actual discovery of gaseous ammonia was made by Priestley (1774), when he collected the gas, evolved by the action of lime upon sal-ammoniac, by means of his mercurial pneumatic trough. Priestley named the gas *alkaline air*.

Occurrence.—In combination as ammonium carbonate it is present in small quantities in the air, derived by the decay of nitrogenous animal and vegetable matter. As nitrate and nitrite it is found in rain-water. It is evolved, along with boric acid, from the fumaroles of Tuscany (see Boric Acid), and is found as ammonium chloride and sulphate in the vicinity of active volcanoes.

Modes of Formation.—(1.) Ammonia can be synthetically produced by submitting a mixture of nitrogen and hydrogen to the influence of the silent electric discharge (Donkin). The amount of ammonia so obtained, however, is extremely small, and can best be shown by passing the gases, as they issue from the "ozone tube," through a cylinder containing a small quantity of Nessler's solution.[*] In a short time the solution will begin to show a yellowish-brown colour, indicating the presence of traces of ammonia.

(2.) Ammonia may be prepared by gently heating any of the ammonium salts, with either of the caustic alkalies, potash or soda, or with slaked lime. The salt most commonly employed is the chloride. When this is mixed with an excess of slaked lime, and the mixture gently heated in a flask, ammonia is evolved, and calcium chloride and water are formed—

$$2NH_4Cl + CaH_2O_2 = CaCl_2 + 2H_2O + 2NH_3.$$

The gas may be dried by being passed through a cylinder containing lumps of quicklime,[†] and may then be collected either by upward displacement or in the mercurial trough. On account of its extreme solubility it cannot be collected over water.

(3.) Ammonia is formed by the action of nascent hydrogen upon salts of nitrous and nitric acid, thus—

$$NaNO_3 + 4H_2 = NaHO + 2H_2O + NH_3.$$

This method is often made use of in the quantitative estimation of nitrates in drinking water.

(4.) When nitrogenous organic matter is subjected to destructive distillation, that is, strongly heated out of contact with air, ammonia is formed; hence when coal, which usually contains about 2 per cent. of nitrogen, is distilled in the process of the manufacture of ordinary illuminating gas, one of the products of the decomposition is ammonia. The "ammoniacal liquor" of the gas works is the source of all ammonia salts at the present day. The liquor is boiled with milk of lime, and the ammonia thus expelled is absorbed by sulphuric acid. The ammonium sulphate so obtained is purified by recrystallisation.

Properties.—Ammonia is a colourless gas, having a powerfully pungent smell, and a strong caustic taste. It is lighter than air, its density being 0.589 (air = 1). Ammonia possesses the property of alkalinity in a very high degree; it turns red litmus blue, and yellow turmeric brown. The gas is unable to support combustion,

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[*] A solution of mercuric iodide in potassium iodide, rendered alkaline with potassium hydroxide.

[†] The usual desiccating agents, namely, sulphuric acid, or phosphorus pentoxide, are inadmissible in the case of ammonia, as this gas at once unites with such compounds.

and is irrespirable. Under ordinary conditions ammonia is not combustible, but if the air be heated or if the amount of oxygen be increased the gas will then burn with a flame of a characteristic yellow-ochre colour. This behaviour of ammonia as regards combustibility is most conveniently illustrated by means of the apparatus shown in Fig. 56. A stream of the gas obtained by gently heating a quantity of the strong aqueous solution in a small flask is delivered through a tube which is surrounded by a wider glass tube. Through the cork which carries this tube a second tube passes, through which a supply of oxygen can be passed. On applying a lighted taper to the jet of ammonia as it issues from the tube it will be noticed that the gas burns in the heated air round the flame of the taper, but is unable to continue burning when the taper is withdrawn. If now a gentle stream of oxygen be admitted into the annular space between the two tubes the ammonia readily ignites, and continues to burn with its characteristic flame. On cutting off the supply of oxygen the flame of the burning ammonia languishes and dies out.

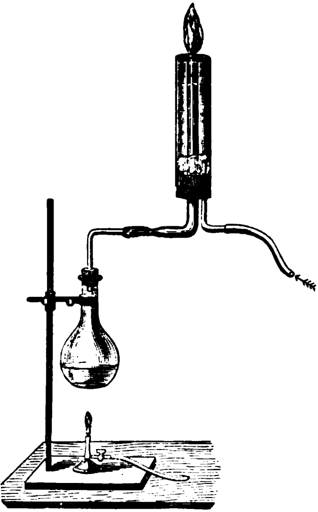


FIG. 56.

Ammonia is extremely soluble in water ; 1 c.c. of water at 0° C., and at the standard pressure, dissolves 1148 c.c. of ammonia, measured at 0° C. and 760 mm. The solubility rapidly decreases as the temperature rises, as will be seen by the following table :—

1 c.c. of Water at 760 mm. Dissolves	Grammes, NH_3.	c.c. at 0° C. and 760 mm.
At 0°	0.875	1148
„ 8°	0.713	923
„ 16°	0.582	764
„ 30°	0.403	529
„ 50°	0.229	306

When a solution of ammonia is heated the gas is rapidly evolved, and at the boiling temperature the whole of it is given up.

The great solubility of this gas in water may be shown by filling a large bolt-head flask with ammonia by displacement, the flask being closed by means of a cork through which a long tube passes, as shown in Fig. 57. On removing the cork from the end of the tube water slowly rises until it reaches the top, and as soon as the first drops enter the globe the absorption proceeds with great rapidity, the water being forced up the tube in the form of a fountain, which continues until the flask is filled.

FIG. 57.

Commercial *liquor ammoniæ* is prepared by passing ammonia gas into water; the strongest solution has a specific gravity of 0.882 at 15°, and contains 35 per cent. of ammonia. During the process of solution heat is liberated, and when the gas is again expelled the same amount of heat is reabsorbed. If a rapid stream of air be driven through a quantity of strong ammonia solution, contained in a glass flask, the ammonia gas is quickly expelled; and if the flask be placed upon a wooden block, as seen in Fig. 58, upon which a few drops of water have been poured, it will be found that after a few moments the flask will have become firmly frozen to the block. By the rapid evaporation of ammonia in this way it is possible to lower the temperature to −40° C.

Ammonia is an easily liquefiable gas; thus at 15.5° it requires a pressure of 6.9 atmospheres, and at 0° only 4.2 atmospheres, in order to liquefy it. The gas was first liquefied by Faraday (1823) by heating in one limb of a closed and bent glass tube (see Fig. 2) a quantity of a compound of ammonia with silver chloride, the other limb of the tube being immersed in a freezing-mixture. The experiment may be made in a tube constructed as seen in Fig. 59. The wide limb is nearly filled with dry precipitated silver chloride which has been saturated with ammonia gas. This compound melts at about 38°, and at a somewhat higher temperature it gives up its ammonia. If the narrow limb of the tube be immersed in a freezing-mixture while the compound is being heated, the combined influence of the cold and the pressure exerted by the evolved ammonia will cause the gas to liquefy and collect in the cold portion of the tube. On removing the tube from the freezing-mixture and allowing the other end to cool, the liquid ammonia will boil off and be reabsorbed by the silver chloride, reforming the original compound.

Liquid ammonia is easily obtained in larger quantity by passing the gas through a glass tube immersed in a bath of solid carbonic acid and ether. Liquid ammonia is a colourless, mobile, and highly refracting liquid, boiling at $-33.7°$, and having a specific gravity at 0° of 0.6234. When cooled below $-75°$ it solidifies to a mass of white crystals.

Liquid ammonia dissolves the metals sodium and potassium, the solution in each case being of an intense blue colour. On the evaporation of the liquid the metal is deposited unchanged.

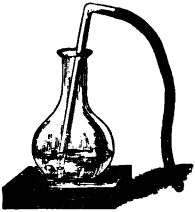


FIG. 58.

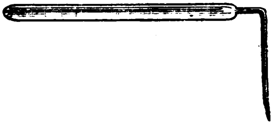


FIG. 59.

During the evaporation of liquid ammonia, boiling as it does at so low a temperature as $-33.7°$, a rapid absorption of heat takes place, and as this substance is so easily obtained it was one of the earliest liquids employed for the artificial production of ice. Various ice-making machines have been invented by M. Carré, in which the reduction of temperature required is obtained by the evaporation of liquid ammonia.

Ammonia is decomposed into its elements at a temperature below a red heat. In this decomposition two volumes of ammonia give one volume of nitrogen and three volumes of hydrogen. The gaseous products, therefore, obtained by passing ammonia through a red-hot tube are inflammable. In the same way, when electric sparks are passed through ammonia, the gas is resolved into its constituents. By performing this experiment upon a measured volume of ammonia confined in a eudiometer over mercury, it will be found that after the passage of the sparks for a short time and the readjustment of the levels of mercury, the original volume of the gas has been doubled.

The fact that the hydrogen and nitrogen are present in ammonia in the proportion of three volumes of hydrogen to one of nitrogen can be shown by taking advantage of the fact that ammonia is decomposed by chlorine, the latter combining with the hydrogen to form hydrochloric acid and the nitrogen being set free. This is effected by means of the apparatus shown in Fig. 60. The long glass tube, divided into three equal divisions, is filled with chlorine and closed by a cork carrying a small dropping funnel. A few cubic centimetres of strong aqueous ammonia are poured into the funnel and allowed to enter the tube drop by drop. As the first two or three drops fall into the chlorine it will be seen that the combination is attended with a feeble flash of light, and fumes of ammonium chloride are formed. When the reaction is complete the whole of the chlorine will have combined with hydrogen derived from the ammonia to form hydrochloric acid, and this in its turn will combine with the excess of ammonia added, forming ammonium chloride. This substance dissolves in the water. A small quantity of dilute sulphuric acid is next introduced by means of the dropping funnel in order to absorb the remaining excess of ammonia. The atmospheric pressure is then once more restored by attaching to the funnel a bent tube, dipping into a beaker of water, as shown in the figure, and when the water is allowed to enter it will be found to flow into the tube until it reaches the second graduation. The gas which is left and which occupies one of the divisions of the tube is found on examination to be nitrogen. This one measure of nitrogen, therefore, has been eliminated from that amount of ammonia which has been decomposed by the chlorine with which the tube was originally filled. Now chlorine combines with its own volume of hydrogen, therefore the volume of hydrogen which was in combination with the one measure of

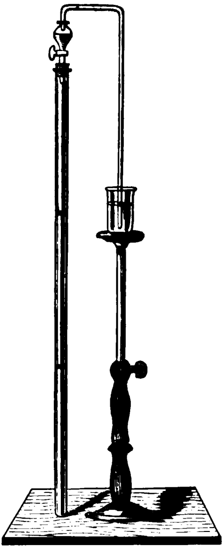


FIG. 60.

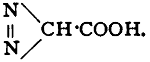
nitrogen is equal to the volume of chlorine contained in the tube, that is to say, it was three measures. We have, therefore, one measure of nitrogen and three measures of hydrogen, or, in other words, ammonia is a combination of nitrogen and hydrogen in the proportion of one volume of nitrogen to three volumes of hydrogen.

In contact with many metals at a moderately high temperature ammonia is decomposed into its elements, and a compound of the metal with nitrogen is formed. In this way, at temperatures ranging between about 400° and 800° a number of metallic nitrides have been obtained.* These compounds are produced by passing a rapid stream of ammonia gas through heated porcelain tubes containing the metal in the form of either wire, foil, or fine powder. When heated in an atmosphere of hydrogen, these nitrides are decomposed into nitrogen and the respective metal, hence they can only be produced in the presence of a large excess of ammonia gas.

Ammonia combines directly with acids forming salts, known as ammonium salts, in which the nitrogen functions as a pentad element; thus with hydrochloric and sulphuric acids it forms respectively ammonium chloride and ammonium sulphate—

$$NH_3 + HCl = (NH_4)Cl.$$
$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

(The ammonium salts will be described with the compounds of the alkali metals.)

Hydrazine (*diamidogen*), $NH_2 \cdot NH_2$ or N_2H_4.—This compound was first prepared by Curtius (1887). It is obtained from a salt of an organic acid known as diazo-acetic acid,  $\overset{N}{\underset{N}{\|}} > CH \cdot COOH$. When the ethereal salt of this acid is acted upon by potassium hydroxide, the potassium salt of another acid is formed, namely triazo-acetic acid. This we may regard as merely a polymer of the first acid, and represent its formula $(N_2 : CH \cdot COOH)_3$. When this compound is digested with dilute sulphuric acid it is converted into hydrazine sulphate and oxalic acid. Thus, employing the simple formula for the acid—

$$N_2 : CH \cdot COOH + H_2SO_4 + 2H_2O = N_2H_4H_2SO_4 + H_2C_2O_4.$$

Hydrazine may also be prepared from purely inorganic sources. When hydrogen potassium sulphite is acted upon by potassium nitrite, a compound known as potassium dinitroso-sulphonate is produced, $O : N \cdot N \cdot OK \cdot KSO_3$.

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* Beilby and Henderson, *Jour. Chem. Soc.*, November 1901.

The mechanism of the reaction will be made clearer if the formula for the nitrite be written $O:N\cdot OK$. Thus—

$$2O:N\cdot OK+2HKSO_3=O:N\cdot N\cdot OK\cdot KSO_3+K_2SO_4.$$

By the action of nascent hydrogen (from sodium amalgam) at the temperature of ice, this compound is converted into the potassium salt of hydrazine sulphonate—

$$O:N\cdot N\cdot OK\cdot KSO_3+6H=H_2N\cdot NH\cdot KSO_3+KHO+H_2O.$$

And this compound on distillation with potassium hydroxide yields hydrazine—

$$H_2N\cdot NH\cdot KSO_3+HKO=H_2N\cdot NH_2+K_2SO_4.$$

The base itself may also be obtained by heating together in a sealed tube, to a temperature of 170°, hydrazine hydrate, N_2H_4,H_2O, and barium monoxide. Under these circumstances the barium oxide takes up the water from the hydrazine hydrate, according to the equation—

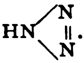
$$BaO+N_2H_4H_2O=Ba(HO)_2+N_2H_4.$$

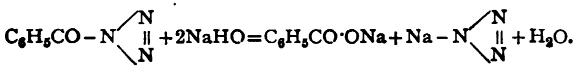
When the tube is opened, the gaseous hydrazine, which is under considerable pressure, rushes out of the tube, forming dense fumes in contact with the atmospheric moisture, with which it combines with great readiness.

Hydrazine Hydrate, $N_2H_4H_2O$.—The compound formed by the combination of hydrazine with water is obtained by distilling hydrazine sulphate, $N_2H_4H_2SO_4$, with an aqueous solution of potassium hydroxide (caustic potash) in a vessel of silver. It is a colourless, fuming, powerfully corrosive liquid, which boils at 118.5°. It attacks glass, cork, and indiarubber, and can only be prepared in vessels of silver or platinum which are screwed together at their junctions. With the halogen acids it forms two series of salts, in which either one or two molecules of the halogen acid are present: thus with hydrochloric acid we have—

Hydrazine monohydrochloride . . .	N_2H_4HCl.
Hydrazine dihydrochloride	N_2H_42HCl.

Hydrazine and its salts act as powerful reducing agents, and give the characteristic red precipitate of cuprous oxide when added to Féhling's solution. This reaction serves to immediately distinguish these compounds from ammonium salts.

Hydrazoic Acid or Azoimide, HN_3 or  $HN\left<\begin{matrix}N\\ \| \\ N\end{matrix}\right.$.—Discovered by Curtius (1890). The sodium salt is prepared by boiling benzoylazo-imide with sodium hydroxide, when sodium benzoate and sodium hydrazoate are formed, thus—



$$C_6H_5CO-N\left<\begin{matrix}N\\ \| \\ N\end{matrix}\right.+2NaHO=C_6H_5CO\cdot ONa+Na-N\left<\begin{matrix}N\\ \| \\ N\end{matrix}\right.+H_2O.$$

It is also produced when sodamide (obtained by heating sodium in dry ammonia gas) is heated to 200° in a stream of nitrous oxide*—

$$2NH_2Na+N_2O=NaN_3+NaHO+NH_3.$$

The sodium hydrazoate so obtained is then gently warmed with dilute sulphuric acid, when sodium sulphate and hydrazoic acid are formed, thus—

$$2NaN_3+H_2SO_4=Na_2SO_4+2HN_3.$$

Properties.—This compound is a colourless volatile liquid, boiling at 37°. The vapour possesses a most unpleasant and powerfully penetrating odour. If inhaled, even when largely diluted with air, it exerts an irritating action upon the mucous membrane. As its name denotes, it is an acid substance, and in many of its properties it strongly resembles the halogen acids. The compound is extremely soluble in water, and forms a strongly acid liquid which smells of the vapour. This solution when boiled, finally assumes a definite strength, and yields on distillation an aqueous acid of constant composition, in this respect resembling aqueous hydrochloric acid, *q.v.*

In its constitution this acid may be compared with hydrocyanic acid, and with the halogen acids—

$$H(N_3);\ H(CN);\ H(Cl);\ H(Br),$$

in which the radical cyanogen (CN), or the halogen elements, Cl and Br, are replaced by the group consisting of three nitrogen atoms.

When a solution of hydrazoic acid is added to a solution of silver nitrate, a white precipitate of silver hydrazoate is formed, strongly resembling silver cyanide and silver chloride in appearance. This silver salt, however, is not acted upon by light in the way the chloride is, and it differs also in being extremely explosive. A minute quantity of the compound, when touched with a hot wire, detonates violently.

This instability and tendency to explode is characteristic of the acid and most of its salts. The sodium salt, however, may be heated to about 250° before it decomposes.

When gaseous hydrazoic acid is mixed with gaseous ammonia, dense white fumes are formed, consisting of ammonium hydrazoate. These two hydrides of nitrogen, apparently so similar, but in reality so widely different, unite to form the ammonium salt, just as gaseous hydrochloric acid and ammonia combine to form ammonium chloride, thus—

$$NH_3+H(N_3)=NH_4(N_3).$$
$$NH_3+HCl=NH_4Cl.$$

The *alkaline* hydride of nitrogen, ammonia, combines with the *acid* hydride of nitrogen, hydrazoic acid, and forms the salt ammonium hydrazoate NH_4N_3 or N_4H_4.

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* See Experiment 298, "Chemical Lecture Experiments," new. ed.

HYDROXYLAMINE.

Formula, $NH_2(OH)$.

Discovered by Lossen in 1865.

Modes of Formation.—(1.) By the action of nascent hydrogen upon nitric oxide, nitric acid, or certain nitrates—

$$2NO + 3H_2 = 2NH_2(OH).$$
$$HNO_3 + 3H_2 = 2H_2O + NH_2(OH).$$

The nascent hydrogen is evolved from tin and hydrochloric acid, and a stream of nitric oxide passed through the mixture. The hydrochloride of hydroxylamine is thus obtained. This is purified by first passing a stream of sulphuretted hydrogen through the solution. The tin is thus precipitated as sulphide, and is removed by filtration. The filtered solution is then evaporated to dryness, and the hydrochloride of hydroxylamine is dissolved out of the residue by means of absolute alcohol, in which solvent ammonium chloride is only very slightly soluble. The alcohol is then distilled off, and the residue is converted into the sulphate by being treated with the requisite quantity of sulphuric acid. Hydroxylamine itself, in aqueous solution, is obtained from the sulphate by the addition of baryta-water.

(2.) By boiling potassium hydroxylamine disulphonate with water for several hours—

$$2N(OH)(SO_3K)_2 + 4H_2O = (NH_3OH)_2SO_4 + 2K_2SO_4 + H_2SO_4.$$

The potassium sulphate is removed by crystallisation.

Properties.—Hydroxylamine is known only in aqueous solution. The solution is colourless, and has an alkaline character. When the solution is distilled the substance is partially decomposed. The solution is a powerful reducing agent; it precipitates gold and mercury from their solutions, and reduces cupric salts, throwing down the red cuprous oxide on being boiled.

Hydroxylamine is a base, and may be regarded as ammonia, in which one of the hydrogen atoms has been replaced by the monad group *hydroxyl* (OH). Like ammonia it unites with acids forming salts, without the elimination of water.

$$NH_2OH + HCl = NH_3OHCl \text{ (or } NH_2OH,HCl).$$
$$2NH_2OH + H_2SO_4 = (NH_3OH)_2SO_4 \text{ (or } 2NH_2OH,H_2SO_4).$$

The salts of hydroxylamine all decompose on the application of heat, with a more or less sudden and violent evolution of gas; thus the nitrate breaks up with almost explosive violence into nitric oxide and water—

$$NH_2OH{\cdot}HNO_3=2NO+2H_2O.$$

AMMON-SULPHONATES.

These compounds may be regarded as derived from ammonia, by the gradual replacement of the hydrogen by the group SO_3H or SO_2OH.

Ammon-sulphonic acid . . .	$NH_2(SO_3H)$.
Ammon-disulphonic acid . .	$NH(SO_3H)_2$.
Ammon-trisulphonic acid . .	$N(SO_3H)_3$.

Potassium ammon-trisulphonate is precipitated as a crystalline salt when excess of a solution of potassium sulphite is added to a solution of potassium nitrite—

$$3K_2SO_3+KNO_2+2H_2O=4KHO+N(SO_3K)_3.$$

Prolonged boiling with water converts it first into the ammon-disulphonate—

$$N(SO_3K)_3+H_2O=NH(SO_3K)_2+HKSO_4,$$

and finally into ammon-sulphonate—

$$NH(SO_3K)_2+H_2O=NH_2(SO_3K)+HKSO_4.$$

Ammon-sulphonic acid is a stable crystalline body; the other two acids are only known in their salts.

When an ice-cold solution of sodium nitrite is added to hydrogen sodium sulphite, a compound is obtained which may be regarded as derived from ammon-trisulphonic acid by the replacement of one of the groups, SO_3H, by hydroxyl, OH—

$$NaNO_2+2NaHSO_3=N(OH)(SO_3Na)_2+NaHO.$$

On the addition of a saturated solution of potassium chloride in the cold, the sodium salt is converted into the potassium salt, which slowly crystallises from the solution, with two molecules of water, $N(OH)(SO_3K)_2,2H_2O$.

This potassium hydroxylamine disulphonate is an unstable compound, and on boiling with water the two SO_3K groups are replaced by hydrogen, forming first potassium hydroxylamine monosulphonate, $NH(OH)SO_3K$, and finally hydroxylamine, NH_2OH.

COMPOUNDS OF NITROGEN WITH THE HALOGEN ELEMENTS.

Nitrogen Trichloride, NCl_3.—This compound was discovered by Dulong (1811). Its true composition was proved by Gattermann (1888).

Mode of Formation.—Nitrogen trichloride is obtained by the action of chlorine upon ammonium chloride—

$$NH_4Cl+3Cl_2=NCl_3+4HCl.$$

When a solution of ammonium chloride is electrolysed, the chlorine, which is evolved at the positive electrode, acts upon the ammonium chloride, forming the trichloride of nitrogen.*

Properties.—Nitrogen trichloride is a thin oily liquid, of a pale-yellow colour, and having a specific gravity of 1.65. It is very volatile, and has an unpleasant pungent smell, the vapour being extremely irritating to the eyes. It is the most dangerously explosive compound known, and when suddenly heated, or brought into contact with grease, turpentine, or phosphorus, it at once explodes. It also explodes on exposure to sunlight. At a temperature of 71° it may be distilled, but the operation is one of the utmost danger. Nitrogen trichloride is decomposed by ammonia, forming ammonium chloride and free nitrogen; hence in the preparation of nitrogen by the action of chlorine upon ammonia, the presence of an excess of ammonia prevents the formation of this dangerous compound.

Nitrogen Tribromide, NBr_3.—When potassium bromide is added to nitrogen trichloride beneath water, a red, oily, highly explosive substance is obtained, believed to be the tribromide of nitrogen.

Nitrogen Iodide, $N_2H_3I_3$.—When strong aqueous ammonia is added to powdered iodine, a brown-coloured powder is formed which has violently explosive properties. Also when alcoholic solutions of iodine and of ammonia are mixed, a brown and highly explosive compound is produced.

Curtois, who first prepared the substance, believed it to have the composition NI_3, and this view was held by Gay-Lussac and others. Gladstone and others considered that the substance contained one atom of hydrogen, and that the formula NHI_2 expressed the composition. The investigations of Szuhay (1893) also led him to believe that the compound obtained by the addition of an excess of aqueous ammonia to a concentrated solution of iodine in potassium iodide has the composition NHI_2.

The subject has recently been reinvestigated by Chattaway (*Proc. Chem. Soc.*, 1899), who for the first time appears to have obtained the compound in a state of purity by the addition of ammonia to a solution of potassium hypoiodite. Under these circumstances the substance separates out in the form of well-defined crystals having a composition expressed by the formula $N_2H_3I_3$, which may be regarded either as NI_3,NH_3 or NHI_2,NH_2I. The equations representing the formation of the compound may be thus expressed—

$$KIO+NH_4HO=NH_4IO+KHO,$$
$$3NH_4IO=N_2H_3I_3+NH_3+3H_2O.$$

The reaction which takes place when the compound is obtained by the action of iodine upon strong ammonia appears also to involve the first formation of the unstable ammonium hypoiodite, thus—

$$I_2+2NH_4HO=NH_4IO+NH_4I+H_2O,$$

which then breaks up as shown above.

Properties.—Nitrogen iodide is a copper-coloured glittering crystalline compound, appearing red by transmitted light. In the amorphous state, as obtained by the action of iodine upon strong ammonia, it presents the appearance of

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* See "Chemical Lecture Experiments," new ed., No. 301.

a dark chocolate-brown powder. When moist it may be handled without much risk of explosion, although it has been known to explode even under water. When dry the substance is extremely explosive; the shock caused by the tread of a fly upon it is more than sufficient to explode it; even falling dust particles will sometimes cause it to explode.

When nitrogen iodide is placed in dilute aqueous ammonia, and exposed to bright light, it is decomposed, and bubbles of nitrogen are seen escaping from the compound—

$$N_2H_3I_3 = N_2 + 3HI,$$

the hydriodic acid being neutralised by the ammonia present. At the same time a *small* quantity of the compound is converted into ammonium hypoiodite, which being unstable slowly passes into the iodate, thus—

$$N_2H_3I_3 + 3H_2O + NH_3 = 3NH_4IO,$$
$$3NH_4IO = NH_4IO_3 + 2NH_4I.$$

CHAPTER VIII

CARBON

Symbol, C. Atomic weight = 12.00.

Occurrence.—This element is capable of assuming three allotropic forms, and it occurs free in nature in each of these modifications, viz., diamond, graphite, and charcoal.

In combination with oxygen, carbon occurs in carbon dioxide, a gas which is present in the air, being a constant product of combustion and respiration. In combination with hydrogen it occurs as marsh gas. Carbon is a constituent of all the natural carbonates, such as limestone, dolomite, &c., which form an important fraction of the earth's crust, and it is also an essential constituent of all organic substances.

DIAMOND.

Occurrence.—This substance has been known and prized from the remotest antiquity. It is found in various parts of India, mostly in river gravels and superficial deposits, in Brazil, South Africa, Australia, and various parts of the United States. The diamond has also recently been obtained from extra-terrestrial sources. In a meteorite which fell in Russia on September 22, 1886, carbon was found, partly as amorphous and partly as adamantine carbon.

The diamond form of carbon is found of various colours ; sometimes it is dark grey, or even black, stones of these colours being known as carbonado and bort. The former of these is extremely hard, and is of great value for use in rock-boring and drilling instruments. Bort is used in the crushed condition by lapidaries for grinding and polishing.

Occasionally the diamond is found coloured blue, or red, or green by traces of foreign materials. Some of these coloured stones are of great value as gems: the well-known "Hope" diamond, a stone weighing 44½ carats, has a fine sapphire colour.

The origin of the diamond is unknown, although many theories have been put forward to explain its formation. Newton's famous suggestion, that diamond was "an unctuous substance coagulated," was based upon its remarkably high refractive index. The cellular structure which is sometimes to be seen in the ash that is left when the diamond is burnt seems to indicate that it is of vegetable origin.

Modes of Formation.—Innumerable attempts have been made to effect the crystallisation of carbon in the adamantine form; but while it is readily possible to convert this variety of carbon into its allotropes graphite and charcoal, the transformation of these back again to the diamond is a problem that is beset with the greatest difficulties. Moissan has recently shown * that the carbon, which is capable of being dissolved in molten iron, and which is usually deposited in the graphitic form on cooling, can, under certain conditions, be caused to take up the adamantine form.

By raising the temperature of the iron to about 3000° by means of an electric furnace, and then suddenly cooling the molten mass by plunging the crucible into water or molten lead, until the cooled and solidified surface is at a dull red heat, an enormous pressure is brought to bear upon the interior and still liquid portion. Under these circumstances, a part of the carbon which is deposited by the slowly cooling mass was found by Moissan to be in the adamantine form. On dissolving the iron in hydrochloric acid, amongst the carbonaceous residue were found fragments having a specific gravity between 3.0 and 3.5, and sufficiently hard to scratch ruby. Some of the fragments were the black or carbonado variety, while others were transparent. On combustion in oxygen, Moissan proved that these were really carbon in the diamond form.

Properties.—The diamond in its purest condition is a colourless crystalline substance. Its crystalline forms belong to the cubic system, and appear to some extent to be characteristic of the locality in which the element occurs. It is extremely hard and moderately brittle. When struck with a hammer the diamond not only splits along its cleavage-planes, but also in other directions, with a conchoidal fracture. It does not conduct electricity. The

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* *Comptes Rendus de l'Académie des Sciences*, vol. cxvi. p. 218.

specific gravity of diamond varies slightly in different specimens, the mean being about 3.5. Its refractive index is higher than that of any other substance, and it is this property which gives its peculiar beauty and brilliancy to the cut stone.

The value of diamond as a gem depends largely upon its colourlessness, except in the case of those rare instances where the colour is quite definite and also pleasing, such as distinct red, blue, or green.

When diamond is strongly heated it becomes black, and increases in bulk, being converted into a substance having the properties of coke. Lavoisier (1772) was the first to show that the diamond was a combustible body, and that it yielded carbon dioxide. Davy (1814) showed that carbon dioxide was the only product of its combustion, and proved that diamond was pure carbon.

The combustion of diamond in oxygen may readily be accomplished by means of the apparatus shown in Fig. 61. A fragment of diamond is supported upon a small gutter of platinum foil, which bridges across two stout copper wires, A. These wires pass through a cork in a perforated glass plate, and are lowered into a cylinder of oxygen. By the passage of an electric current the little platinum boat can be strongly heated, when the diamond will become ignited, and continue to burn brilliantly in the oxygen, with the formation of carbon dioxide. The ash, which is always left after a diamond has been burnt, varies from 0.2 to 0.05 per cent. of the stone. It is found usually to contain ferric oxide and silica.

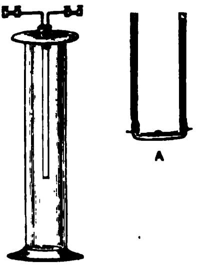

FIG. 61.

GRAPHITE.

Occurrence.—This second allotrope of carbon is much more plentiful in nature than the first. It is found in large quantities in Siberia, Ceylon, and various parts of India. In England the chief source of graphite has been the mines at Borrowdale in Cumberland; this supply is now practically exhausted. Enormous quantities of very pure graphite are now obtained from the Eureka Black-Lead Mines in California. Graphite also occurs in many specimens of meteoric iron.

Mode of Formation.—Molten iron, especially when it contains silicon, is capable of dissolving a considerable amount of carbon, which, on cooling, is deposited in the form of black shining crystals of graphite. Occasionally considerable quantities of graphite are found deposited in this way in iron-smelting furnaces, to which the name "kish" has been applied.

Graphite is now manufactured by heating a mixture of 97 parts of amorphous carbon (charcoal or coke) and 3 parts of iron in an electric furnace. It was formerly believed that at the high temperature of the electric arc amorphous carbon was converted directly into the graphitic modification; but it has recently been shown (Acheson) that *pure* charcoal does not by itself undergo this transformation; that the change, in reality, takes place through the intermediate formation of a metallic carbide. The product obtained is practically free from iron, as the metal is volatilised at the high temperature.

Properties.—Graphite is a soft, shiny, greyish-black substance, which is smooth and soapy to the touch. It is usually found in compact laminated masses, but sometimes crystallised in six-sided plates. Its specific gravity varies in different specimens, averaging about 2.5. Graphite is a good conductor of both heat and electricity.

When strongly heated in oxygen, graphite takes fire and burns, forming carbon dioxide, and leaving an ash consisting of silica, alumina, and oxide of iron. Graphite has been found by Regnault to contain, usually, traces of hydrogen. Graphite is employed for the manufacture of ordinary lead pencils; for, on account of its softness, it leaves a black mark upon paper when drawn across it. For the purposes of the pencil manufacture the natural graphite is ground to powder and carefully washed free from gritty matter. It is then mixed with the finest washed clay, and the pasty mass is forced by hydraulic pressure through perforated plates. The name "graphite," from the Greek *to write*, is given to this substance on account of its use for this purpose. It was formerly supposed that this material contained lead, hence the names *black-lead* and *plumbago.*

When powdered graphite is subjected to prolonged treatment with boiling nitric acid and potassium chlorate it undergoes partial oxidation, and is converted into a greyish crystalline substance which was termed by its discoverer (Brodie) *graphitic acid.* It contains carbon, hydrogen, and oxygen, and is believed to have a composition represented by the formula $H_4C_{11}O_5$. When heated, this compound undergoes a very curious transformation. If a fragment about the size of a pea is heated in the bottom of a test-tube, feeble signs of visible combustion are seen, and a light, porous black mass is produced which fills and overflows the tube. This porous mass appears to be pure *graphite*. At the same time a little moisture condenses upon the tube.

Graphite is largely employed, on account of its refractoriness, for the manufacture of the so-called plumbago crucibles, which consist of fireclay mixed with finely-ground graphite.

Other uses to which graphite is put are for glazing or polishing gunpowder, especially the larger grained varieties ; as a lubricant for machinery, where oil is inadmissible on account of high temperature ; for electrotyping processes, and also as a coating for ironwork, to prevent rusting.

AMORPHOUS CARBON.

This non-crystalline form of carbon may be obtained by the decomposition of a great variety of carbon compounds, by the process known as destructive distillation. The carbon so obtained differs very much as regards its purity, according to the particular organic compound used for its preparation. The commonest forms of amorphous carbon to be met with are lampblack or soot, gas carbon, coke, charcoal, animal charcoal or bone-black. None of these substances is pure carbon ; animal charcoal, for example, usually containing only about 10 per cent. of carbon.

Lampblack.—This substance is manufactured by burning substances rich in carbon, and which burn with a smoky flame (as turpentine, petroleum, or tar), with a limited supply of air. The smoke is passed into chambers in which are suspended coarse blankets, upon which the soot collects. The lampblack always contains hydrogen in the form of hydrocarbons. If the soot be heated to redness in a stream of chlorine, this hydrogen can be removed, and pure amorphous carbon will be left.

Lampblack is used for printers' ink and for black paint.

Gas Carbon.—This form of carbon is obtained by the destructive distillation of coal in the manufacture of illuminating gas. It remains in the retorts as an extremely hard deposit, lining the roof and sides. It is a very pure carbon, coming second to purified lampblack. Its specific gravity is about 2.35. Gas carbon is a good conductor of electricity, and is extensively used for the manufacture of carbon rods for the arc light.

Coke.—This substance differs from gas carbon, although it also is obtained in the process of coal distilling. It contains all the inorganic matter which constitutes the ash of the coal, and also small quantities of hydrogen, nitrogen, and oxygen. The average amount of carbon in coke is about 91 per cent.

Charcoal.—The purest form of charcoal is obtained by the carbonisation of pure white sugar and the subsequent ignition of the charcoal in a stream of chlorine gas. Charcoal so obtained has a specific gravity of 1.57. Charcoal in a much less pure condition is manufactured from wood. The methods by which the carbonisation of wood is carried out are, broadly, of two kinds: first, those in which access of air is permitted to the burning material; and, second, those in which air is excluded.

The first of these, and the most ancient, is generally carried on in more primitive parts, where wood is plentiful. The wood is piled into mounds or stacks, which are built with some care. They are set on fire in the interior by means of a lighted bundle of brushwood, which is introduced through a vertical opening or chimney, left for this purpose in the centre of the mound during its construction. The outside of the heap is covered with brushwood, and finally with turf, in order to regulate the access of air to the interior, and therefore to control the rate of combustion of the wood. The object of the charcoal-burner is to carbonise the wood as slowly as possible. In this process there is great liability to loss, by the too rapid combustion of the wood; and, in addition, it possesses the disadvantage that the secondary products, such as the pyroligneous acid, tar, &c., are entirely lost.

Various modifications have been introduced into the method of *coaling* wood, as the process is termed, with a view to collect these products.

In the second general process of carbonising wood, the material is heated in ovens or retorts from the outside, no air being admitted to the wood. The operation is very similar to that employed in the destructive distillation of coal, in the manufacture of coal gas. In these methods all the volatile and condensable products are collected; among these are water, pyroligneous acid, wood spirit, acetone, and fatty oils. The non-condensable products consist mainly of such gases as hydrogen, carbon monoxide, carbon dioxide, marsh gas, and acetylene.

Animal Charcoal.—Bone-black is obtained by the carbonisation of bones in iron retorts. This variety of charcoal is the least pure of all the ordinary forms of amorphous carbon.

Bone contains only about 30 per cent. of organic matter, the other 70 per cent. consisting chiefly of calcium phosphate, associated with small quantities of magnesium phosphate and calcium carbonate. It will be obvious, therefore, that as the carbon is derived from the organic matter, the amount of it in carbonised bones must be small. The average composition of animal charcoal is found to be—

Carbon	10.0
Calcium phosphate	88.0
Other saline substances	2.0
	100.0

Although containing relatively so small an amount of carbon, animal charcoal possesses many of the valuable properties of charcoal in a highly marked degree, owing to the fact that it contains its carbon disseminated throughout an extremely porous mass of calcium phosphate.

Properties of Charcoal.—Charcoal varies very considerably in its properties, depending upon the particular wood from which it is obtained, and the method by which it is prepared. Thus, charcoal obtained at 300° is a soft, brownish-black, very friable material, having an igniting point as low as 380°. On the other hand, charcoal prepared at very high temperatures is black and comparatively dense, and requires to be strongly heated in order to ignite it.

Under ordinary circumstances, charcoal burns in air without the formation of a flame, or the production of smoke. At high temperatures, however, the combustion of charcoal is seen to be attended by a flame. This is probably accounted for by the fact, that as the temperature at which the combustion of carbon takes place is raised above 700°, the amount of carbon monoxide which is formed increases, and the carbon dioxide decreases.*

When charcoal is thrown upon water it floats, on account of the air which is enclosed within its pores. The specific gravity of charcoal when thus filled with air varies from 0.106 (charcoal made

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* Ernst, *Chemisches Repertorium*, vol. xvii. p. 2.

from the ash) to 0.203 (charcoal from the birch). If the air be withdrawn from charcoal it sinks in water, the average specific gravity of charcoal itself being 1.5.

Ordinary charcoal is a bad conductor of electricity, but its conductivity is greatly increased by strongly heating the charcoal in closed vessels.

Charcoal has the power of absorbing gases and vapours to a remarkable extent: this power, which is exhibited to a different degree by the various kinds of charcoal, is due to the porosity of the material, whereby it exposes a very large surface; and it belongs to a class of phenomena known as *surface action.*

If a fragment of charcoal, recently strongly heated to expel the air from its pores, be passed up into a cylinder of ammonia gas, standing in a trough of mercury, the ammonia will be gradually absorbed by the charcoal, and the mercury will ascend in the cylinder. Saussure found that recently heated beech-wood charcoal was capable of absorbing ninety times its own volume of ammonia gas; while Hunter, by employing charcoal made from cocoa-nut shell, found that 171.7 volumes of ammonia were absorbed by 1 volume of charcoal. The results of both of these experiments show that those gases are absorbed in the largest quantities which are the most readily liquefiable. The gas so held by the charcoal is in a highly condensed condition upon the surface of the porous mass. Probably in the case of easily liquefied gases, such as ammonia, sulphur dioxide, and others, the gases are partially liquefied upon the surface of the charcoal. In this condensed state the gas is more chemically active than under ordinary conditions, and charcoal is therefore able to induce many striking combinations to take place. Thus, if charcoal be allowed to absorb chlorine, and dry hydrogen be then passed over it, the chlorine is capable of combining with the hydrogen even in the dark, with the formation of hydrochloric acid. This chemical activity of gases, when absorbed by charcoal, is strikingly exemplified in the case of sulphuretted hydrogen. If a quantity of powdered charcoal, which has been saturated with sulphuretted hydrogen, be brought into oxygen, the rapid combination of the two gases is attended with the development of so much heat that the charcoal bursts into active combustion. In the same way a mixture of air, with 10 or 15 per cent. of sulphuretted hydrogen, may be passed rapidly through a tube, about a metre in length, filled with charcoal, without a trace of sulphuretted hydrogen escaping at the end.* Owing to this property charcoal is largely employed to absorb noxious gases, the atmospheric oxygen which is condensed in the pores of the charcoal oxidising these offensive and injurious compounds; thus sewer ventilators are often trapped with a layer of charcoal, which effectually arrests all bad-smelling gases.

Charcoal also has the power of absorbing colouring matters from solution: thus, if water which has been tinted with an organic colouring matter be shaken up with powdered charcoal and filtered, the solution will be found to be entirely decolourised. The variety of charcoal which possesses this property in the highest degree is animal charcoal, or bone-black, and this substance is largely employed in many manufacturing processes, such as sugar-refining, in order to remove all colouring matter from the liquid.

Charcoal under ordinary conditions is unacted upon by the air, but when the temperature is raised it enters into active combustion, forming carbon dioxide. In an extremely divided condition, however, carbon is capable of combining spontaneously with the oxygen of the air, and with so much energy as to take fire.

Coal.—The carbonaceous minerals that are included under the name *coal* are an impure form of carbon, containing compounds of carbon with hydrogen and oxygen. Coal is the final result of a series of decomposition changes which have been undergone by vegetable matter of the remote past, the process having extended over long geological periods. During this prolonged process a portion of the carbon and hydrogen is eliminated as marsh gas, and large quantities of this gas are found associated with, and occluded in, coal.

Broadly speaking, the numerous varieties of coal may be divided into *soft* or *bituminous*, and *hard* or *anthracitic*.

The former are employed for the manufacture of coal gas and for ordinary domestic purposes; they burn with a smoky flame, and evolve large quantities of gases and volatile vapours on combustion or distillation. Anthracite coal is much harder, ignites with more difficulty, and burns with the formation of very little flame or smoke. It contains a higher percentage of carbon, and gives out great heat on combustion, and is employed largely as a steam-coal.

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* "Chemical Lecture Experiments," 394–396, new ed.

The following table shows the average composition of coals from various sources, and the general difference between coals of the two main classes :—

Locality.		Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Ash.	Water.	Coke.
Bituminous.	Northumberland	81.41	5.83	7.90	2.05	0.74	2.07	1.35	66.70
	Wales . .	83.78	4.79	4.15	0.98	1.43	4.91	..	72.60
	Staffordshire .	78.57	5.29	12.88	1.84	0.39	1.03	11.29	57.21
Anthracite.	S. Wales . .	92.56	3.33	2.53	...	...	1.58	...	...
	Pennsylvania .	90.45	2.43	2.45	...	...	4.6	...	...

CHAPTER IX

CARBON COMPOUNDS

THE compounds of the element carbon are so numerous that it has been found convenient to constitute the study of these substances a separate branch of chemistry. In the early history of the science it was believed that there were a large number of substances which could only be obtained as the product of living organisms. They were known to be elaborated by the action of life, or, as it was termed, the *vital force*, and it was believed that owing to some inherent specific quality belonging to this vital force the substances produced by its action were distinct from such substances as could be prepared by any laboratory processes. To denote this distinction, the term *organic* was applied to those things which were known to be the products of living organisms, and other compounds were distinguished as *inorganic* substances. This distinction received its deathblow in 1828, when Wöhler produced, by purely laboratory processes, one of the most typical of all organic compounds, namely, urea. The names "organic" and "inorganic" chemistry are still retained, but their old significance is entirely gone, as no distinction is to-day recognised between products elaborated by the action of life and those which can be synthetically produced.

Speaking broadly, organic chemistry may be described as the chemistry of the carbon compounds. Nevertheless, although it is quite true that all "organic compounds" contain carbon, it has not been found expedient to include in the category of organic compounds *all* compounds containing carbon. Not because there is any intrinsic difference in these compounds, but merely from considerations of convenience. The following may be mentioned as examples of such compounds as are not regarded as belonging to the "organic" division: compounds of carbon with the metals, namely, the so-called *carbides*, of which cast iron and calcium carbide are familiar cases; the compounds of carbon with sulphur and the extensive series of thio-carbonates ; carbon monoxide and the compounds formed by its direct union with non-metals (*e.g.* carbonyl chloride, &c.) and with metals (*e.g.* nickel carbonyl, &c.) ; and lastly, carbon dioxide and all the multitude of metallic carbonates. Obviously, therefore, the broad distinction above mentioned must not be regarded as a *definition.* Indeed, it may be said that no exact definition of an "organic" compound has ever been framed, and we have to accept the general statement that "organic" chemistry is the chemistry of the carbon compounds with certain generally acknowledged exceptions.

Amongst the compounds of carbon which will be briefly treated of in these chapters, there will be included three which all chemists agree to regard as organic substances : these are methane (marsh gas), CH_4 ; ethylene, C_2H_4 ; and acetylene, C_2H_2. These three compounds play an important part in our ordinary illuminating flames and in coal gas.

COMPOUNDS OF CARBON WITH OXYGEN.

Two oxides of carbon are known, both of which are colourless gases, viz. :—

Carbon monoxide	CO.
Carbon dioxide	CO_2.

CARBON MONOXIDE.

Formula, CO. Molecular weight=28. Density=14.

Modes of Formation.—(1.) Carbon monoxide is formed when carbon dioxide is passed over charcoal heated to bright redness—

$$CO_2+C=2CO.$$

The same result is obtained when a slow stream of air or oxygen is passed over red-hot charcoal contained in a tube. The first action of the air on coming in contact with the carbon is to form carbon dioxide, which, passing over the remainder of the heated material, is deprived of a portion of its oxygen according to the above equation. This operation goes on in an ordinary fire-grate: the air, on first gaining access to the burning coal or coke, causes the complete oxidation of a portion of the carbon to carbon dioxide; and as this gas passes through the mass of red-hot carbon it is reduced to the lower oxide, which either escapes with the other products of combustion or becomes ignited and burns with a lambent bluish flame such as may frequently be noticed upon the top of a " clear " fire.

(2.) When steam is passed over strongly heated carbon a mixture of carbon monoxide and hydrogen is produced. This mixture, known as *water gas*, is employed in many manufacturing processes as a gaseous fuel—

$$H_2O + C = CO + H_2.$$

(3.) Carbon monoxide is also formed by the action of carbon dioxide upon red-hot iron—

$$4CO_2 + 3Fe = Fe_3O_4 + 4CO.$$

(4.) Or by strongly heating either carbon or iron with a carbonate, such as calcium carbonate, which is capable of yielding carbon dioxide, thus—

$$CaCO_3 + C = CaO + 2CO.$$
$$4CaCO_3 + 3Fe = Fe_3O_4 + 4CaO + 4CO.$$

(5.) Carbon monoxide is most conveniently prepared, by the decomposition of certain organic compounds by means of sulphuric acid. Thus, when formic acid, or a formate, is acted upon by sulphuric acid, the sulphuric acid withdraws the elements of water from the molecule of formic acid, and leaves carbon monoxide—

$$H{\cdot}COOH - H_2O = CO.$$

(6.) By a similar decomposition, oxalic acid yields a mixture of carbon monoxide and carbon dioxide in equal volumes—

$$C_2H_2O_4 - H_2O = CO_2 + CO.$$

The carbon dioxide is readily removed from the mixture, by passing the gases through a solution of sodium hydroxide (caustic soda), in which carbon dioxide is absorbed with the formation of sodium carbonate.

(7.) The method usually employed when carbon monoxide is required for experimental purposes consists in heating a mixture of one part by weight of crystallised potassium ferrocyanide (yellow prussiate of potash) with ten parts of strong sulphuric acid in a capacious flask, when the following reaction takes place—

$$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

The six molecules of water required by the reaction are derived partly from the acid employed and partly from the salt, which contains three molecules of water of crystallisation.*

Properties.—Carbon monoxide is a colourless, tasteless gas, having a faint smell. It is only slightly soluble in water, its coefficient of absorption at 0° being 0.03287. It burns in the air with a characteristic pale-blue flame, forming carbon dioxide—

$$2CO + O_2 = 2CO_2.$$

When mixed with half its own volume of oxygen, and inflamed, the mixture explodes with some violence.† If the two gases be confined in a eudiometer standing over mercury, and be rendered absolutely free from aqueous vapour by powerful desiccating agents, no explosion will take place upon the passage of an electric spark through the mixture. And in the same way, if carbon monoxide, which has been deprived of all aqueous vapour, be burned from a jet in the air, and the jet be lowered into a cylinder containing air which has been similarly dried, the flame will be extinguished (see page 191).

Carbon monoxide is an extremely poisonous gas: very small quantities present in the air rapidly give rise to headache and giddiness, and if inhaled for a length of time, or if taken into the lungs in a less dilute condition, insensibility and death quickly follow. The deaths that have resulted from the use of unventilated fires—either of charcoal or coke, or in some cases of coal gas—in dwelling-rooms, have been due to the escape of this poisonous gas into the air. The extremely deadly nature of the *after-damp* resulting from a colliery explosion is due to the presence of carbon monoxide in the carbon dioxide which is formed as a product of the combustion.

The poisonous action of this gas is due to its absorption by the blood, with the formation of a bright red compound, to which the name *carboxy-hæmoglobin* is applied. Blood so charged appears to be unable to fulfil its function of absorbing and distributing oxygen throughout the system. This carboxyhæmoglobin gives a characteristic absorption spectrum, which furnishes a ready method of detection in cases of poisoning from the inhalation of carbon monoxide.

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* "Chemical Lecture Experiments," new ed., 435–439.

† The rate at which the combustion is propagated throughout a mixture of carbon monoxide and oxygen is much slower than through hydrogen and oxygen. Bunsen has estimated it at less than 1 metre per second.

Carbon monoxide is one of the most difficultly liquefiable gases, its critical temperature being −136°.

At high temperatures this gas is a powerful reducing agent, uniting with another atom of oxygen to form carbon dioxide. This fact is made use of in many metallurgical processes for reducing the oxides of the metals to the metallic state.

Carbon monoxide is absorbed at ordinary temperatures by a solution of cuprous chloride, forming the compound $COCu_2Cl_2$.

At a temperature of boiling water, carbon monoxide is slowly absorbed by solid potassium hydroxide, with the formation of potassium formate—

$$KHO + CO = H{\cdot}COOK.$$

Carbon monoxide unites directly with chlorine, under the influence of sunlight, forming the compound known as *phosgene gas*, or carbonyl chloride—

$$CO + Cl_2 = COCl_2.$$

If the two gases are mixed in equal volumes, and kept in the dark, no action takes place, but on exposure to sunlight they combine, and the yellowish colour due to the chlorine will disappear. On opening the vessel in moist air, clouds of hydrochloric acid are formed, owing to the decomposition of carbonyl chloride by the moisture, according to the equation—

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

Carbonyl chloride may be readily condensed to a liquid, its boiling-point being + 8°.

Carbon monoxide unites directly with certain metals, giving rise to compounds which possess some very remarkable properties, and to which the name *metallic carbonyls* has been applied by their discoverer.*

When carbon monoxide is allowed to stream slowly over metallic nickel (obtained by the reduction of nickel oxide in a stream of hydrogen), the gas is absorbed by the finely-divided metal, forming a compound having the composition $Ni(CO)_4$. If the issuing gas be passed through a cooled tube, the nickel carbonyl condenses to a colourless, mobile, highly refracting liquid, having a specific gravity at 0° of 1.356, and boiling at 43° under a pressure of 751 mm.†

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* Mond, 1890.

† See "Chemical Lecture Experiments," new ed., 446–448.

Nickel carbonyl vapour burns with a luminous flame, which produces a black deposit of metallic nickel when a cold porcelain dish is depressed upon the flame. The gas is decomposed into nickel and carbon monoxide if passed through a hot glass tube, the nickel being deposited as a bright metallic mirror upon the glass—

$$Ni(CO)_4 = 4CO + Ni.$$

A similar compound of carbon monoxide and iron has also been obtained, having the composition $Fe(CO)_5$. Iron carbonyl is a pale-yellow, viscous liquid, boiling at 102.8° under a pressure of 749 mm. Its specific gravity at 18° is 1.4664. When heated to 180° the vapour is decomposed, iron being deposited and carbon monoxide being evolved. This compound has been found in iron cylinders in which the so-called *water gas* (a mixture of H and CO) has been stored under pressure for a length of time; it is also said to be present in minute quantities in coal gas.

CARBON DIOXIDE.

Formula, CO_2. Molecular weight = 44. Density = 22.

History.—Van Helmont in the seventeenth century was the first to distinguish between this gas and ordinary air: he observed that it was formed during the processes of combustion and fermentation, and he applied to it the name *gas sylvestre.* Black showed that this gas was a constituent of what in his day were known as the *mild alkalis* (alkaline carbonates), and on account of its being so combined, or fixed, in these substances, he named the gas *fixed air.* Lavoisier first proved its true chemical composition to be that of an oxide of carbon.

Occurrence.—Carbon dioxide is a constant constituent of the atmosphere, being present to the extent of about 3 volumes in 10,000 volumes of air. It is also found in solution in all spring-water, which is sometimes so highly charged with this gas under pressure that the water is effervescent, or "sparkling," from the escape of the gas. Carbon dioxide is evolved in large quantities from vents and fissures in the earth in volcanic districts. The well-known Poison Valley in Java, which is an old volcanic crater, and the Grotto del Cane near Naples, owe their peculiar properties to the discharge into them of large quantities of carbon dioxide from such subterranean sources.

Modes of Formation.—(1.) Carbon dioxide* is produced when carbon is burnt with a free supply of air or oxygen—

$$C + O_2 = CO_2.$$

If an insufficient supply of oxygen be employed, carbon monoxide is produced at the same time.

(2.) When limestone or chalk is strongly heated, as in the process of burning lime, carbon dioxide is evolved in large quantities—

$$CaCO_3 = CaO + CO_2.$$

(3.) In the ordinary processes of fermentation, and during the decay of many organic substances, carbon dioxide is also formed. Thus, when sugar undergoes alcoholic fermentation by means of yeast, the sugar is converted into alcohol and carbon dioxide—

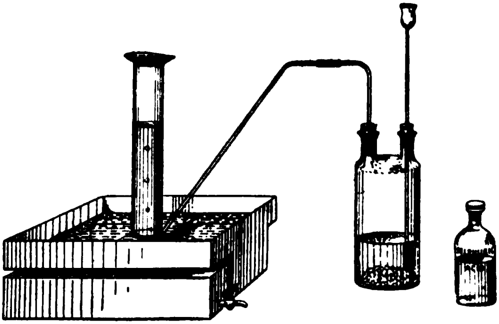

FIG. 62.

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_6O + 4CO_2.$$

(4.) Carbon dioxide is formed during the process of respiration ; also by the combustion of all ordinary fuels, and of any compound containing carbon, such as candles, oils, gas, &c.

(5.) For experimental purposes, carbon dioxide is most readily obtained by the decomposition of a carbonate by means of a stronger acid. The effervescence that results from the action of tartaric acid upon sodium bicarbonate, in an ordinary Seidlitz

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* Experiments on carbon dioxide, Nos. 400–434, "Chemical Lecture Experiments," new ed.

powder, is due to the disengagement of this gas. The most convenient carbonate for the preparation of this gas is calcium carbonate, in one of its many naturally occurring forms, such as marble, limestone, or chalk. Fragments of marble are for this purpose placed in a two-necked bottle (Fig. 62), with a quantity of water, and strong hydrochloric acid is added by means of the funnel-tube. A rapid effervescence takes place owing to the elimination of the gas, and a solution of calcium chloride remains in the bottle—

FIG. 63.

FIG. 64.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

If sulphuric acid be substituted for hydrochloric acid, the fragments of marble rapidly become coated with a crust of insoluble calcium sulphate, which soon prevents the further action of the acid, and therefore puts an end to the reaction : by employing finely powdered chalk, however, instead of lumps of calcium carbonate, this difficulty is obviated. This gas is largely manufactured from these materials.

Properties.—Carbon dioxide is a colourless gas, having a feeble acid taste and a faint and pleasantly pungent smell. It is incapable of supporting either combustion or respiration; a burning taper is instantly extinguished, and an animal speedily dies when introduced into this gas. Although carbon dioxide is not such a poisonous compound as the monoxide, it nevertheless does exert a direct poisonous effect upon the system, and death caused by this gas is not merely due to the absence of oxygen. The prolonged inhalation of air containing only a very slightly increased amount of carbon dioxide has a distinctly lowering effect upon the vitality.

Carbon dioxide is a heavy gas, being about one and a half times heavier than air. On this account it may readily be collected by displacement. By virtue of its great density it may be poured from one vessel to another, much in the same way as an ordinary liquid: thus, if a large bell-jar be filled with the gas by displacement, a beaker-full may be drawn up, as water from a well (Fig. 63). If the gas so drawn up be poured into a similar beaker, suspended from the arm of a balance, and counterpoised, the weight of the gas will be evident by the disturbance of the equilibrium of the system.

If a soap bubble be allowed to fall into a large jar filled with carbon dioxide, it will be seen to float upon the surface of the dense gas (Fig. 64). The power of carbon dioxide to extinguish flame is so great, that a taper will not burn in air in which this gas is present to the extent of 2.5 per cent., and in which the oxygen is reduced to 18.5 per cent. For this reason a comparatively small quantity of carbon dioxide, brought into the air surrounding a burning body, is capable of extinguishing the flame. This property has been put to valuable service in the construction of numerous contrivances for extinguishing fire, such as the "extincteur." This is a metal vessel containing carbon dioxide under pressure, the gas having been generated within the closed apparatus by the action of dilute sulphuric acid upon sodium carbonate. A stream of the gas, projected judiciously upon a moderate conflagration in a dwelling, readily extinguishes the fire. This property may be illustrated by inflaming a quantity of turpentine in a dish, and pouring upon the flames a quantity of carbon dioxide contained in a large bell-jar (Fig. 65), when it will instantly extinguish the conflagration.

Although carbon dioxide is incapable of supporting combustion in the ordinary sense, certain metals are capable of burning in this gas. Thus, a fragment of potassium when heated in this gas burns brightly, forming potassium carbonate with the deposition of carbon—

$$2K_2 + 3CO_2 = 2K_2CO_3 + C.$$

When carbon dioxide is passed into a solution of calcium hydroxide (lime water) a turbidity at once results, owing to the precipitation of insoluble calcium carbonate or chalk—

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

This reaction furnishes the readiest means for the detection of carbon dioxide. Thus, if the gas obtained by any of the modes of formation described be passed into clear lime water, the formation of this white precipitate of chalk is proof that the gas is carbon dioxide. By this test it may readily be shown that carbon dioxide is a product of respiration, by merely causing the exhaled breath to bubble through a quantity of lime water, which will quickly be rendered turbid.

FIG. 65.

Carbon dioxide is moderately soluble in water. At the ordinary temperature water dissolves about its own volume of this gas.

The coefficient of absorption at 0° is 1.7967, the solubility decreasing with rise of temperature in accordance with the interpolation formula—

$$c = 1.7967 - 0.07761t + 0.0016424t^2.$$

Carbon dioxide shows a slight departure from Henry's law (see page 143), when the pressures are greater than that of the atmosphere. Thus, when the pressure is doubled, the amount dissolved is slightly more than doubled. The solubility of carbon dioxide in water, and its increased solubility under pressure, is illustrated in the ordinary aerated waters. Water under a pressure of several atmospheres is saturated with the gas, and upon the release of this pressure by the withdrawal of the cork the excess of gas, over and above that which the water can dissolve at the ordinary pressure, escapes with the familiar effervescence. In a similar manner the natural aerated waters have thus become charged with carbon dioxide, under subterranean pressure, and when such waters come to the surface the dissolved gas begins to make its escape.

The solution of carbon dioxide in water is feebly acid, turning blue litmus to a port-wine red colour, characteristically different from the scarlet red given by stronger acids. This acid may be regarded as the true carbonic acid—

$$CO_2 + H_2O = H_2CO_3.$$

A recently-made sample of aerated water is seen to effervesce more briskly and give off the dissolved gas more rapidly than specimens that have been long preserved. In process of time the dissolved carbon dioxide gradually combines with the water, with the formation of carbonic acid, an unstable compound which slowly decomposes into carbon dioxide and water, especially at a slight elevation of temperature. Many of the naturally occurring aerated waters, such as Apollinaris, when opened exhibit scarcely any effervescence, but give off carbon dioxide gradually. Such waters have in all probability been exposed to pressure for a great length of time, and their dissolved carbon dioxide has almost entirely combined to form carbonic acid. When such a water is gently warmed a rapid stream of gas is evolved.

When carbon dioxide is strongly heated, as by the passage of electric sparks, it is partially dissociated into carbon monoxide and oxygen. This decomposition is never complete; for when the amount of these two gases in the mixture reaches a certain proportion, they reunite to form carbon dioxide, and a point of equilibrium is reached when as many molecules are united as are dissociated in the same time.

Liquid Carbon Dioxide.—Carbon dioxide is easily liquefied.

At −5° it requires a pressure of 30.8 atmospheres; at +5°, 40.4 atmospheres; while at +15° a pressure of 52.1 atmospheres is required.

Faraday first liquefied this gas, by introducing into a strong bent glass tube a quantity of sulphuric acid and a few lumps of ammonium carbonate, which were prevented from touching the acid by means of a plug of platinum foil. The tube was then hermetically sealed, and the acid allowed gently to come in contact with the carbonate, which was at once decomposed with the formation of ammonium sulphate and carbon dioxide. By the internal pressure exerted by the evolved gas, aided by the application of cold to one end of the bent tube, the gas condensed to a colourless liquid.

Large quantities of this liquefied gas were obtained by Thilorier by a precisely similar method, the experiment being performed in strong wrought-iron vessels.

Liquid carbon dioxide is to-day manufactured on a large scale, by pumping the gas into steel cylinders by means of powerful compression pumps. The enormous volumes of carbon dioxide evolved in the process of brewing, and which until quite recently were allowed to escape into the atmosphere, are now utilised for this purpose. The gas, as it is evolved from the fermenting vats, is washed and purified, and pumped into steel bottles for the market. In this form the gas is largely employed by manufacturers of aerated waters, and also as the refrigerating agent in "cold storage."

Liquid carbon dioxide is a colourless and extremely mobile liquid, which floats upon water without mixing. It boils at −80° under atmospheric pressure.

When heated, liquid carbon dioxide expands at a more rapid rate than a gas, its coefficient of expansion being greater than that of any known substance. Its rapid change of volume is seen by the following figures:—

95 volumes at −10° become
100 „ „ 0° „
106 „ „ +10° „
114 „ „ +20°

The critical temperature of carbon dioxide is 31.35°. If the liquid be heated to this point, it passes into the gaseous state without any change of volume. The line of demarcation between the liquid and gas in the tube gradually fades away, and the tube appears filled with gas. Above this temperature no additional pressure is able to liquefy the gas. On once more cooling the tube, when the critical point is passed the liquid again appears, and the dividing line between it and the gas is once more sharply defined.

Solid Carbon Dioxide.—When liquid carbon dioxide is allowed to escape into the air the absorption of heat due to its rapid evaporation causes a portion of the liquid to solidify. This solid is most conveniently collected by allowing the jet of liquid to stream into a round metal box (Fig. 66), in which it is caused to revolve by being made to impinge upon the curved tongue of metal. The box is furnished with hollow wooden handles, through which the gas makes its escape. Considerable quantities of the frozen carbon dioxide can in this way be collected in a few minutes.

On a larger scale the brass box is substituted by a canvas bag, which is simply tied over the nozzle of the cylinder containing the liquefied gas, and a rapid stream of the liquid allowed to escape into it.

Solid carbon dioxide is a soft, white, snow-like substance. When exposed to the air it quickly passes into gas, without going through the intermediate state of liquidity.

Solid carbon dioxide is readily soluble in ether, and this solution constitutes one of the most convenient sources of cold. A large number of gases can readily be liquefied by being passed through tubes immersed in this freezing-mixture. When this ethereal solution is rapidly evaporated its temperature can be lowered to -110°.

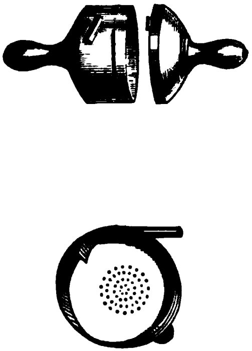

FIG. 66.

"Carbonic acid snow," as this substance is sometimes termed, is now an article of commerce, the compound being sent into the market in this form to avoid the cost of the carriage of the necessarily heavy steel bottles containing the liquid.

Composition of Carbon Dioxide.—When carbon burns in oxygen, the oxygen undergoes no change in volume in being transformed into carbon dioxide. The volume of carbon dioxide produced is the same as that of the oxygen which is required for its production. This may be shown by means of the apparatus (Fig. 67).

The bulb of the U-tube is filled with oxygen, and the stopper, which carries a small bone-ash crucible upon which a fragment of charcoal is placed, is lowered into position. The charcoal is ignited by means of a thin loop of platinum wire, as shown in the figure, which can be heated by an electric current. As the carbon burns the heat causes a temporary expansion of the included gas; but after the combustion is complete and the apparatus has cooled, the level of mercury will be found to be undisturbed. Carbon dioxide, therefore, contains its own volume of oxygen. From this experiment the composition of carbon dioxide by weight can be deduced. One litre of carbon dioxide weighs 22 criths; deducting from this the weight of 1 litre of oxygen, viz., 16 criths, we get 6 as a remainder. Six parts by weight of carbon, therefore, combine with 16 parts by weight of oxygen to form 22 parts of carbon dioxide: expressing this proportion atomically, the proportion of carbon to oxygen is 12 to 32.

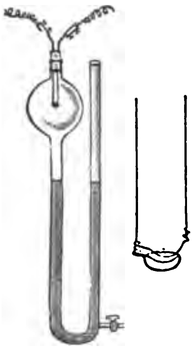

FIG. 67.

The gravimetric composition of carbon dioxide may be directly determined by the combustion of a known weight of pure carbon in a stream of oxygen gas, and absorbing and weighing the carbon dioxide that is formed. This was done with great care and accuracy by Dumas and Stas in the experiments by which they determined the atomic weight of carbon. Fig. 68 represents the apparatus employed for this purpose. A weighed quantity of diamond, contained in a small platinum boat, was introduced into a porcelain tube, which could be strongly heated in a furnace. The oxygen for its combustion was contained in a glass bottle, from which it could be expelled by allowing water to enter through the funnel. As it was necessary that the oxygen should be absolutely free from any carbon dioxide, the water used in the little gas-holder contained potassium hydroxide in solution. The oxygen was then passed through the tubes A, B, C, in order to deprive it of carbon dioxide and moisture, and lastly through a small desiccating tube, *d*, which was weighed before and after the experiment. The pure dry oxygen then entered the strongly heated tube, and the carbon there burnt away to carbon dioxide, leaving a minute quantity of ash, which was carefully weighed at the conclusion of the experiment. A small layer of copper oxide was placed in the tube, in the position indicated in the figure, in order to oxidise any traces of carbon monoxide which were liable to be formed into the dioxide. The product of the combustion was carried forward by the stream of oxygen through a series of tubes ; *d′* is a small weighed desiccating tube, the weight of which, if the diamond used contained no hydrogen, should remain unchanged. It then passes through the bulbs F and G, where the carbon dioxide is entirely absorbed. To arrest aqueous vapour, which would be carried away from the solution in these bulbs by the escaping oxygen, the gas is passed through H, containing fragments of solid potassium hydroxide ; this tube is weighed along with the potash bulbs. K is a guard tube containing fragments of solid potassium hydroxide, in order to prevent atmospheric carbon dioxide and moisture from gaining access to the weighed portions of the apparatus.

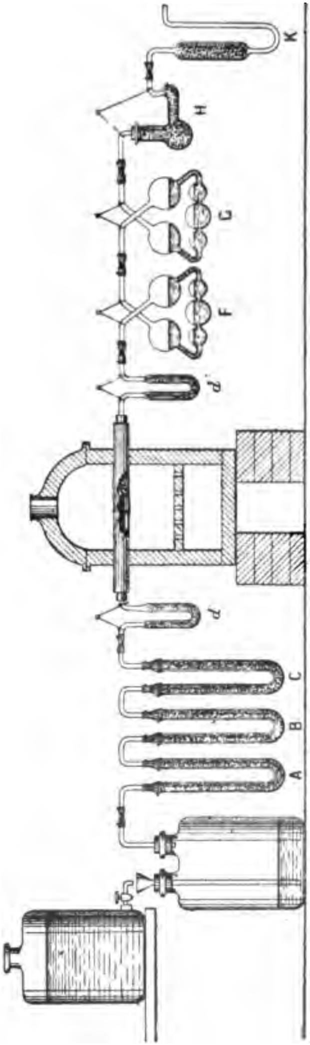

FIG. 68.

The weight of the diamond *minus* the weight of the ash which was left gave the actual weight of the carbon burnt ; the increase in weight of the tubes gave the weight of the carbon dioxide which was produced, and this weight, *minus* the weight of carbon used, gave the weight of oxygen that was consumed. As a mean of a number of experiments, Dumas and Stas found that 80 parts of oxygen by weight combined with 29.99 parts of carbon.

From a knowledge of the density of carbon dioxide and the volume of oxygen it contains, we know that the molecule of this gas contains two atoms; therefore, by the simple equation—

$$80 : 32 :: 29.99 : 11.99,$$

11.99 parts of carbon combine with 32 parts of oxygen, and the number 11.99 is therefore the atomic weight of carbon as determined by these chemists.

The Carbonates.—Although carbonic acid, H_2CO_3, is a very unstable compound, the salts it forms are stable. Being a dibasic acid, it is capable of forming salts in which either one or both of the hydrogen atoms have been replaced by an equivalent of a metal; thus in the case of sodium we have—

(1) Disodium carbonate (normal sodium carbonate) . Na_2CO_3.
(2) Hydrogen sodium carbonate (bicarbonate of soda) . $HNaCO_3$.

Similarly, with the divalent metal calcium, it is possible to form—

(1) Normal calcium carbonate . . . . $CaCO_3$,

and—

(2) Hydrogen calcium carbonate (bicarbonate of lime) . $CaH_2(CO_3)_2$.

The formation of carbonates by the action of carbon dioxide upon the hydroxides may be illustrated by the following equations:—

$$2KHO + CO_2 = K_2CO_3 + H_2O.$$
$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

The first of these changes is the one that takes place when carbon dioxide is absorbed by the potassium hydroxide employed by Dumas and Stas in the course of their experiments already described. The second equation represents the reaction which results when carbon dioxide is passed into lime water. In this latter case, if the gas be passed through the turbid solution for some time, the turbidity will gradually disappear, and the solution once more become clear. The normal calcium carbonate ($CaCO_3$) which is first formed, and which is insoluble, is converted into the soluble bicarbonate, $CaH_2(CO_3)_2$. If this solution be boiled, this unstable salt is decomposed with the evolution of carbon dioxide and water and the reprecipitation of the normal calcium carbonate—

$$CaH_2(CO_3)_2 = CaCO_3 + H_2O + CO_2.$$

The presence of this compound in natural waters is associated with the property known as the *hardness* of water (see Natural Waters, p. 221).

When one volume of dry carbon dioxide is mixed with two volumes of dry ammonia, the two gases unite, forming a compound known as ammonium carbamate—

$$CO_2 + 2NH_3 = CO_2,2NH_3 \text{ or } \left.\begin{matrix} NH_2 \\ NH_4O \end{matrix}\right\} CO,$$

which is the ammonium salt of the unknown carbamic acid, $\left.\begin{matrix} NH_2 \\ HO \end{matrix}\right\} CO$.

The relation between this compound and carbamide or urea will be obvious by an inspection of the formula $\left.\begin{matrix} NH_2 \\ NH_2 \end{matrix}\right\} CO$.

This substance was the first "organic" compound which was ever obtained from purely inorganic sources (page 295). It can be obtained by the action of carbonyl chloride upon ammonia—

$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl.$$

CHAPTER X

COMPOUNDS OF CARBON WITH HYDROGEN

THESE two elements unite together in various proportions, forming an enormous number of compounds known generally under the name of the *hydrocarbons.* The reason for the existence of so great a number of compounds of these two elements is to be found in the fact that the atoms of carbon possess, in a very high degree, the property of uniting amongst themselves. This property of carbon gives rise to the formation of a number of groups or series of compounds the members of which are related to each other and to the simplest member of the series. Thus the compound methane, CH_4, is the simplest member, or the "foundation-stone," of a series of hydrocarbons of which the following are the first four :—

Methane . . .	CH_4	Propane . . .	C_3H_8
Ethane. . . .	C_2H_6	Butane . . .	C_4H_{10}

It will at once be seen that each compound differs in composition from its predecessor by an increment of CH_2, and that each may be expressed by the general formula, C_nH_{2n+2}.

Such a series of compounds is known as a *homologous series,* and any one member is called a *homologue* of any other.

In the following chapter the three hydrocarbons, methane, ethylene, and acetylene, will be briefly studied. Each of these is a "foundation-stone," or starting-point, of a series similar to the one already mentioned ; thus—

Methane, CH_4, first member of the C_nH_{2n+2} series of hydrocarbons.
Ethylene, C_2H_4, ,, ,, C_nH_{2n} ,, ,,
Acetylene, C_2H_2 ,, ,, C_nH_{2n-2} ,, ,,

METHANE (*Marsh Gas—Fire-Damp*).

Formula, CH_4. Molecular weight=16.4. Density=8.2.

Occurrence.—Methane is found in the free state in large quantities in nature. It is one of the products of the decompositions which has resulted in the formation of the coal-measures. It is therefore found in enormous quantities in coal mines, where it not only occurs in vast pent-up volumes, under great pressure, which escape with a rushing sound when the coal is being hewn; but it is also occluded within the pores of the coal. Methane is also evolved from petroleum springs.

The name marsh gas has been given to this compound, on account of its occurrence in marshy places by the decomposition of vegetable matter. The bubbles of gas which rise to the surface when the mud at the bottom of a pond is gently disturbed consist largely of marsh gas.

Modes of Formation.—(1.) When a mixture of sodium acetate and sodium hydroxide is strongly heated in a copper retort, sodium carbonate is produced and marsh gas is evolved—

$$CH_3{\cdot}COONa + NaHO = Na_2CO_3 + CH_4.$$

The gas obtained by this reaction always contains more or less hydrogen.

(2.) Pure methane may be obtained by the decomposition of zinc methyl, by means of water—

$$Zn(CH_3)_2 + 2H_2O = ZnH_2O_2 + 2CH_4.$$

(3.) The most convenient method for preparing methane is by the action of zinc-copper couple upon methyl iodide.* For this purpose the zinc-copper couple is placed in a small flask, and a mixture of equal volumes of methyl iodide and methyl alcohol is introduced by means of the stoppered funnel (Fig. 69). The gas is caused to pass through a tube filled with the zinc-copper couple, whereby it is deprived of any vapour of the volatile methyl iodide, and is collected over water in the pneumatic trough.

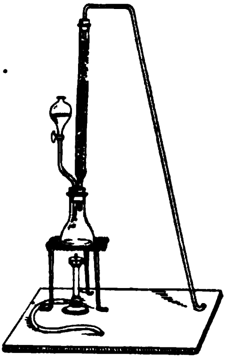

FIG. 69.

The reaction which takes place is essentially a reduction of the iodide by means of the nascent hydrogen produced by the action of the zinc-copper couple upon the alcohol or the water present, and may therefore be represented by the equation—

$$CH_3I + 2H = CH_4 + HI.$$

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* "Chemical Lecture Experiments," new ed., No. 449.

The hydriodic acid must not be regarded as escaping as such, but in the presence of the zinc forming a compound with it. If water only is present, the compound $ZnI{\cdot}HO$ is formed; while if methyl alcohol is employed the zinc compound will have the composition $ZnI{\cdot}CH_3O$: the complete equation (omitting the copper which does not enter into the chemical change) being—

$$CH_3I + Zn + H{\cdot}CH_3O = CH_4 + ZnI{\cdot}CH_3O.$$

Marsh gas is formed during the process of the distillation of coal, and is therefore a large constituent of coal gas, the amount varying from 35 to 40 per cent.

Properties.—Methane is a colourless gas, having no taste or smell. It burns with a pale, feebly luminous flame. When mixed with air or oxygen and ignited the mixture explodes with violence. The products of its combustion are water and carbon dioxide, the methane requiring twice its own volume of oxygen for its complete combustion, and yielding its own volume of carbon dioxide—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Methane is only about one-half as heavy as air, its specific gravity being 0.55 (air = 1). The *fire-damp* of coal mines is nearly pure methane, its average composition being—

Methane	96.0
Carbon dioxide	0.5
Nitrogen	3.5
	100.0

ETHYLENE (*Olefiant Gas*).

Formula, C_2H_4. Molecular weight = 28.4. Density = 14.2.

Modes of Formation.—(1.) This compound is obtained when ethyl iodide is acted upon by an alcoholic solution of potassium hydroxide—

$$C_2H_5I + KHO = KI + H_2O + C_2H_4.$$

(2.) It is also formed when ethylene dibromide is brought in contact with zinc-copper couple, the ethylene dibromide being diluted with its own volume of alcohol—

$$C_2H_4Br_2 + Zn = ZnBr_2 + C_2H_4.$$

(3.) Ethylene may be prepared by acting upon alcohol with certain powerful dehydrating agents, such as phosphoric pentoxide or sulphuric acid, the latter being most commonly employed. The mixture of alcohol and sulphuric acid is heated in a flask to about 165°, when a brisk effervescence takes place. From the point of view of the final products, the reaction may be regarded as the abstraction of the elements of water from the alcohol,* thus—

$$C_2H_6O - H_2O = C_2H_4.$$

The action, however, is always accompanied by secondary reactions, which result in the rapid blackening of the mixture owing to the separation of carbon. The sulphuric acid then acts upon this carbon with the evolution of carbon dioxide and sulphur dioxide. Hence the ethylene that is obtained by this process is always contaminated with considerable quantities of these gases, from which it must be purified by being passed through a solution of sodium hydroxide.

(4.) Pure ethylene is most readily prepared by the action of syrupy phosphoric acid (the ordinary tribasic acid) upon alcohol.† About 50 or 60 c.c. of the acid are placed in a small Wurtz flask of about 180 c.c. capacity. The flask is fitted with a cork carrying a thermometer and a dropping-tube (Fig. 70), the end of the latter being drawn out to a fine point and reaching to the bottom of the flask. The acid is boiled for a few minutes until the concentration reaches such a point that the temperature rises to 200°, when the alcohol is allowed to enter drop by drop; the rate at which the alcohol is admitted being visible in the dropping-bulb. By keeping the temperature between 200° and 220°, a steady and continuous stream of gas is evolved; which after being deprived of the small quantities of ether and undecomposed alcohol with which it is accompanied, by being passed through a small Woulf's bottle standing in ice, is practically pure ethylene. The action of the phosphoric acid is the same as that of sulphuric acid, the first action being the formation of phosphovinic acid, which is subsequently decomposed in a similar manner to the sulphovinic acid.

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* In reality the action is more complex, and takes place in two stages, the first being the formation of ethyl hydrogen sulphate or sulphovinic acid, $C_2H_5{\cdot}HSO_4$—a compound which is analogous to hydrogen potassium sulphate, $KHSO_4$; and the second being the decomposition of this compound when heated either alone or in the presence of sulphuric acid—

$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O,$$
$$C_2H_5{\cdot}HSO_4 = C_2H_4 + H_2SO_4.$$

† Newth, *Jour. Chem. Soc.*, 1901.

Properties.—Ethylene is a colourless gas, having a somewhat pleasant ethereal smell; it burns with a highly luminous flame, forming carbon dioxide and water, one volume of the gas requiring three volumes of oxygen for its complete combustion, and producing twice its own volume of carbon dioxide—

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

If mixed with oxygen in this proportion and inflamed, the mixture explodes with great violence.

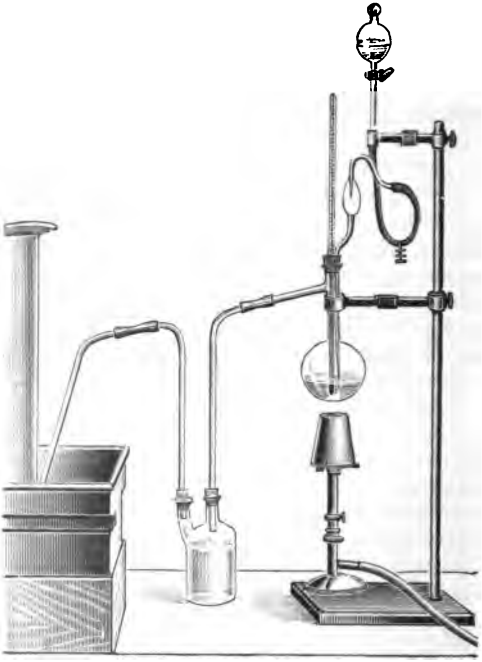

FIG. 70.

When mixed with twice its volume of chlorine and ignited, the mixture burns rapidly with a lurid flame, with the formation of hydrochloric acid and deposition of carbon—

$$C_2H_4 + 2Cl_2 = 4HCl + 2C.$$

Ethylene is rapidly absorbed by fuming sulphuric acid (more slowly by the ordinary strong acid), forming ethyl hydrogen sulphate—

$$C_2H_4 + H_2SO_4 = C_2H_5{\cdot}HSO_4,$$

and from this compound, by distillation with water, alcohol may be produced—

$$C_2H_5{\cdot}HSO_4 + H_2O = C_2H_5{\cdot}OH + H_2SO_4.$$

Ethylene is reduced to the liquid state, at a temperature of 0°, by a pressure of 41 atmospheres; the critical temperature of the gas is +10.1°, at which point a pressure of 51 atmospheres is required to liquefy it. Liquefied ethylene boils at −103°, and by increasing its rate of evaporation temperatures as low as −140° can readily be obtained. Ethylene (together with higher members of the same series) constitutes the chief illuminating constituent of ordinary coal gas, of which it forms from 4 to 10 per cent.

ACETYLENE.

Formula, C_2H_2. Molecular weight=26.2. Density=13.1.

Modes of Formation.—(1.) Acetylene is capable of being synthetically formed by the direct union of its elements. For this purpose a stream of hydrogen is passed through a three-way globe, in which an electric arc is burning between two carbon rods, arranged as seen in Fig. 71 (a quantity of sand being placed in the globe to prevent fracture from falling fragments of red-hot carbon). Under these circumstances a small quantity of the carbon and hydrogen unites to form acetylene, which is swept out of the globe by the current of hydrogen.*

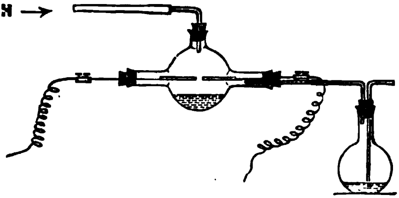

FIG. 71.

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* The formation of acetylene appears to be a secondary result, due to the high temperature decomposition of methane which is first produced (Bone, *Jour. Chem. Soc.*, 1897).

(2.) Acetylene may be obtained by the action of alcoholic potash upon ethylene dibromide. Alcoholic potash is heated in a flask, and ethylene dibromide dropped upon it from a stoppered funnel, when the following reaction takes place—

$$C_2H_4Br_2 + 2KHO = 2KBr + 2H_2O + C_2H_2.$$

(3.) Acetylene is formed when marsh gas or coal gas is burned with an insufficient supply of air for complete combustion; thus, when a Bunsen lamp becomes accidentally ignited at the base of the chimney, the peculiar and unpleasant smell that is perceived is partly, though not entirely, due to the formation of acetylene.

The formation of acetylene by the imperfect combustion of coal gas is readily shown by causing a jet of air to burn in an atmosphere of coal gas, and aspirating the products of combustion through a cylinder containing an ammoniacal solution of cuprous chloride, as shown in Fig. 72. The acetylene is absorbed by the ammoniacal cuprous chloride, forming a deep-red coloured compound known as cuprous acetylide—

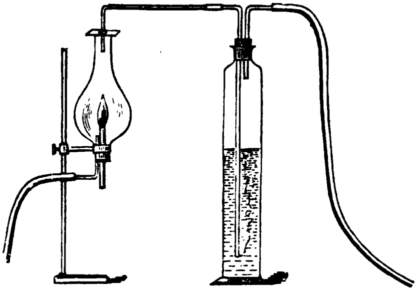

FIG. 72.

$$Cu_2Cl_2,2NH_3 + H_2O + C_2H_2 = 2NH_4Cl + C_2H_2Cu_2O.*$$

When this compound is acted upon by hydrochloric acid, it is decomposed with the evolution of acetylene, thus—

$$C_2H_2Cu_2O + 2HCl = Cu_2Cl_2 + H_2O + C_2H_2.$$

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* Keiser has shown that, when perfectly dry, the compound loses a molecule of water, and has the composition C_2Cu_2, and not $C_2H_2Cu_2O$ (or C_2Cu_2, H_2O); in fact, that the compound is a carbide of copper.

Formerly this method was commonly practised when any quantity of acetylene was required.

(4.) For all practical purposes acetylene is now always prepared by the action of water upon calcium carbide. The carbide may be placed in a dry flask furnished with a dropping funnel and delivery tube, and on gradually admitting water drop by drop a rapid evolution of nearly pure acetylene at once takes place—

$$CaC_2 + 2H_2O = Ca(HO)_2 + C_2H_2.$$

Properties.—Acetylene is a colourless gas having an extremely offensive smell, which rapidly induces headache; when inhaled in an undiluted state it is poisonous. The gas burns with a highly luminous and smoky flame. When burnt from specially constructed jets it gives a pure white light of great intensity, and on this account is a most important illuminant. Acetylene is present in small quantities in ordinary coal gas, and its presence may be detected by the formation of the red precipitate of cuprous acetylide when coal gas is allowed to bubble through an ammoniacal solution of cuprous chloride. This reagent furnishes not only a ready and delicate test for the presence of acetylene, but also provides a means of removing this gas from admixture with other gases. Thus, in the synthetic formation described above, the gases issuing from the globe are passed into a flask containing this solution, which immediately absorbs the acetylene. When acetylene is subjected by prolonged heating to a temperature short of a red heat, it undergoes polymerisation, and is converted into liquid hydrocarbons, of which benzene, C_6H_6, is one.

Nascent hydrogen converts acetylene into ethylene—

$$C_2H_2 + 2H = C_2H_4.$$

From acetylene, therefore (a compound which can be synthetically prepared from its elements, carbon and hydrogen), a great number of "organic" compounds can be built up, for, as has been already explained (page 317), from ethylene it is easy to obtain alcohol, which opens the door to the preparation of a vast number of other organic compounds.

Coal Gas.—When coal is distilled, the volatile products obtained are: (1) coal tar; (2) an aqueous liquid containing ammonia and other products, and known as *ammoniacal liquor*; (3) *coal gas.*

Coal gas, after being subjected to ordinary purification, is a mixture of gases which may be divided into three classes, namely: *illuminants*, *diluents*, and *impurities*. The most important of these substances are—

Illuminants.	Ethylene, C_2H_4; propylene, C_3H_6; butylene, C_4H_8	(C_nH_{2n})	About 6.5 per cent.
	Acetylene, C_2H_2; allylene, C_3H_4 .	(C_nH_{2n-2})	
	Benzene, C_6H_6.	(C_nH_{2n-6})	
Diluents.—Hydrogen, marsh gas, carbon monoxide .			About 90 per cent.
Impurities.—Nitrogen, carbon dioxide, sulphuretted hydrogen			About 3.5 per cent.

The composition of the gas is largely determined by the nature of the coal employed, as may be seen from the following analyses of gas from bituminous and from cannel coal :—

	From Bituminous Coal.		*From Cannel Coal.*	
	London (Frankland).		London (Frankland).	Manchester (Bunsen and Roscoe).
Hydrogen	50.05	51.24	35.94	45.58
Marsh gas	32.87	35.28	41.99	34.90
Carbon monoxide . .	12.89	7.40	10.07	6.64
Illuminants	3.87	3.56	10.81	6.46
Nitrogen	...	2.24	...	2.46
Carbon dioxide . . .	0.30	0.28	1.19	3.67
Sulphuretted hydrogen .	...	...	...	0.29
	100.00	100.00	100.00	100.00

CHAPTER XI

COMBUSTION

WHEN chemical action is accompanied by light and heat, the phenomenon is called *combustion.* All exhibitions of light and heat are not necessarily instances of combustion; thus, when an electric current is passed through a spiral of platinum wire, or through a carbon thread in a vacuous bulb (as in the familiar "glow" lamps), these substances become hot, and emit a bright light. Neither the platinum nor the carbon, however, is undergoing any chemical change, and therefore the phenomenon is not one of combustion. The materials are simply being heated to a state of incandescence by external causes, and as soon as these cease to operate, the glowing substances return to their original condition unchanged.

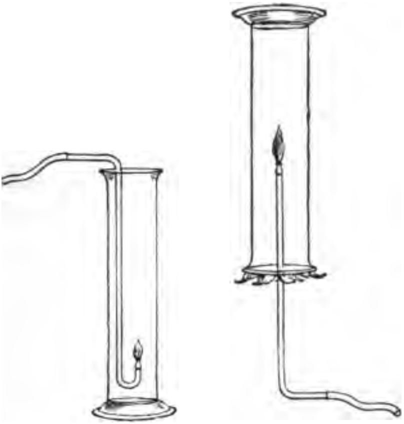
Combustion may be defined as *the chemical union of two substances, taking place with sufficient energy to develop light and heat.* When the amount of light and heat are feeble, the combustion is described as *slow* or *incipient;* while, on the other hand, when they are considerable, the combustion is said to be *rapid* or *active.* The true nature of combustion was not understood until after the discovery of oxygen in 1775. From about the year 1650 until after that important discovery, the phlogistic theory was universally adopted. According to this view, a combustible body was one which contained, as one of its constituents, a substance or *principle* to which the name *phlogiston* was applied. Easily combustible substances were considered to be rich in phlogiston, while those that were less inflammable were held to contain but little of this ingredient. The act of combustion was regarded as the escape of this principle from the burning substance. Thus, when a metal was burnt in the air, it was considered to be giving off its phlogiston, and the material that was left after the combustion (which we now know to be the oxide of the metal) was regarded as the other constituent of the metal, and was called the *calx.* The metal, therefore, was supposed to be a compound of a calx with phlogiston. By heating a calx along with some substance rich in phlogiston, the former again combined with this principle and the metal was once more produced. Thus, when the calx of lead was heated with charcoal (a substance pre-eminently rich in phlogiston), the charcoal supplied the calx with the necessary amount of phlogiston to produce the compound of calx of lead and phlogiston, which was metallic lead. This theory of combustion, after sustaining many severe shocks (from such experiments as those of Boyle and others, who showed that the calx of a metal was *heavier* than the metal used in its formation), received its death-blow on the discovery of the compound nature of water, and that this substance was produced by the combustion of hydrogen in oxygen.

In all processes of combustion it is customary to regard one of the substances taking part in the chemical change as the *combustible*, and the other as the *supporter of combustion*. Usually that substance which surrounds or envelops the other is called the *supporter of combustion*. Thus, when a jet of burning hydrogen is introduced into a jar of chlorine, or when a fragment of charcoal burns in oxygen, the chlorine and the oxygen are spoken of as the *supporters of combustion*, while the hydrogen and carbon are termed the *combustibles*.

In all the more familiar processes of combustion the atmosphere itself is the enveloping medium, and the air is therefore, *par excellence*, the supporter of combustion; and in ordinary language the terms *combustible* and *incombustible* are applied to denote substances which burn, or do not burn, in the air. By a similar process of limitation, it has become customary to speak of other gases as supporters or non-supporters of combustion, if they behave towards ordinary combustibles as air does. Thus we say of hydrogen, or marsh gas, or coal gas, that they are combustible, but do not support combustion; and of oxygen, or chlorine, or nitrous oxide, that they do not burn, but will support combustion; and lastly, of such gases as ammonia, or carbon dioxide, or sulphur dioxide, that they neither burn nor support combustion.

This distinction, however, is a purely conventional one, and has little or no scientific significance; for, by a slight modification of the conditions, either hydrogen, marsh gas, or coal gas may become supporters of combustion, and oxygen, chlorine, or nitrous oxide the combustible substances. Thus, when a jet of hydrogen burns in oxygen, we say that the hydrogen is the combustible, and the oxygen the supporter of combustion (Fig. 73, A); but if a jet of oxygen be thrust up into a jar of hydrogen (Fig. 73, B), it ignites as it passes the burning hydrogen, and continues to burn in the hydrogen.

By means of the apparatus shown in Fig. 74, this may be still more strikingly shown.* A stream of hydrogen is passed into the lamp chimney by the tube H, and the issuing gas inflamed as it escapes at the top. Oxygen is admitted through the tube O, and the jet of gas ignited by pushing the long tube up into the burning hydrogen at the top, and then drawing it down to the position shown in the figure, where the jet of oxygen continues to burn in the atmosphere of hydrogen.



A FIG. 73. B

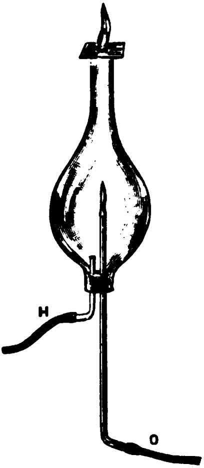


FIG. 74.

By means of the same apparatus, oxygen, or chlorine, or nitrous oxide may be caused to burn in either hydrogen, marsh gas, or coal gas. Ammonia, which, as already mentioned, is usually described as being neither combustible nor a supporter of combustion, when surrounded by an atmosphere of oxygen is readily inflammable, and will as readily support the combustion of oxygen.

The atmosphere itself becomes the combustible body when the

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* "Chemical Lecture Experiments," new ed., No. 367.

usual conditions of combustion are reversed. Thus, if a stream of coal gas be passed through a similar lamp glass, through the cork of which a short straight glass tube passes (Fig. 75), air will be drawn up through this tube, and may be inflamed by passing up a lighted taper. The jet of air will then continue to burn as a non-luminous flame. The air is here the combustible, and the coal gas the supporter of combustion. If the excess of coal gas be inflamed as it escapes from the top, the opposite conditions will be fulfilled, the air being the supporter of combustion, and the coal gas the combustible.

This interchangeableness of the terms combustible and supporter of combustion applies also to substances that are liquid or even solid at the ordinary temperature. If a small quantity of some inflammable liquid, as ether, carbon disulphide, turpentine, &c., be boiled in a flask, and the issuing vapour inflamed, a jet of oxygen gas when lowered into the flask will ignite as it passes the flame, and continue to burn in the vapour of the liquid. In the same way, sulphur, which is a combustible solid, and whose vapour is inflammable in the air, is capable in the state of vapour of supporting the combustion of oxygen. Since combustion is the result of energetic chemical union, and since also it is a mere condition of experiment which of the two acting substances shall function as the environment of the other, it will be seen that the terms "combustible" and "supporter of combustion," as applied to a chemical substance, do not express any definite or characteristic property of that body.

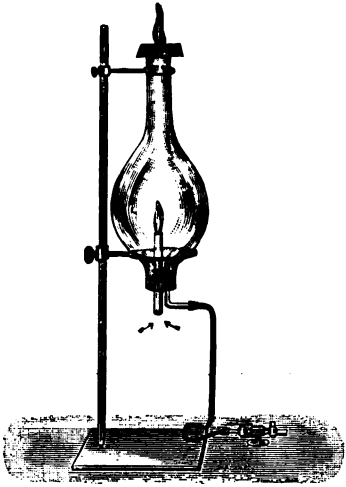
FIG. 75.

It was demonstrated by Boyle, that when a metal is burnt in the air, the calx (or oxide) that is obtained weighs *more* than the metal employed, instead of less, as the phlogistic theory seemed to demand. This fact, which the upholders of phlogiston found it so difficult to reconcile, is seen to be a necessary consequence of combustion, considered from the modern point of view. In all instances of combustion the weight of the products of the action is equal to the total weight of each of the two substances taking part in the chemical combination. When, for example, the metal magnesium burns in the air, the weight of the product of the combustion is equal to the weight of the metal, *plus* the weight of a certain amount of oxygen with which it united in the act of burning. This gain in weight during combustion may be demonstrated in a number of ways. Thus, if a small heap of finely divided iron, obtained by the reduction of the oxide, be counterpoised upon the pan of a balance, and then ignited, the iron will be seen to burn, and as it burns the balance will show that the smouldering mass is increasing in weight. In this case the sole product of the combustion is a solid substance, namely, iron oxide, which remains upon the pan of the balance; but the same result follows when the product of the action is gaseous. Thus, for instance, when a fragment of sulphur is burnt, although it disappears from sight, it, like the iron, combines with oxygen to form an oxide. This oxide, however, being a gas, escapes into the atmosphere. If the sulphur be burnt in such a manner that the sulphur dioxide is collected and weighed, it also will be found to be heavier than the original sulphur. In the process of burning, 1 gramme of sulphur unites with about 1 gramme of oxygen, and the product therefore weighs 2 grammes. By causing an ordinary candle to burn in the apparatus shown in Fig. 76, where the invisible products of its combustion are arrested, the increase in weight may easily be seen. The candle being essentially a compound of carbon and hydrogen, the products of its burning will be carbon dioxide and water, both of which will be absorbed by the

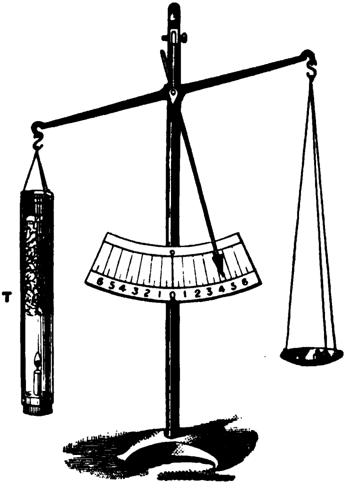

FIG. 76.

sodium hydroxide in the upper part of the tube. Consequently, as the candle burns away, the arrangement gradually gains in weight; the increase being the weight of the atmospheric oxygen which has combined with the carbon and the hydrogen to form the compounds carbon dioxide and water.

Heat of Combustion.—During the process of combustion, a certain amount of heat is evolved, and a certain temperature is attained—two results which are quite distinct. The *temperature* is measured by thermometers or pyrometers, while the *amount of heat* is measured in terms of the *calorie*, or heat unit.*

The amount of heat produced by the combustion of any substance is the same, whether it burns rapidly or slowly, provided always that the same final products are formed in each case. Thus, when 1 gramme of phosphorus burns in the air to form phosphorus pentoxide, it evolves 5747 calories; and when the same weight of phosphorus is burnt in oxygen, although the combustion is much more rapid and energetic, and the *temperature* consequently rises higher, the *amount of heat* evolved is precisely the same.

Again, when iron is heated in oxygen it burns with great brilliancy, and with evolution of much heat; if, however, the same weight of iron be allowed slowly to combine with oxygen, even without any manifestation of combustion, it is found that the *amount of heat* produced in forming the same oxide is absolutely the same.

So far, therefore, as the quantity of heat produced is concerned, there is no difference between *active* combustion and *slow* combustion, or (confining ourselves to the case of combinations with oxygen) between active combustion and the ordinary process of spontaneous oxidation at ordinary temperatures. In the latter case the heat is given out slowly—so slowly that it is conveyed away by conduction and radiation as fast as it is produced, and consequently the *temperature* of the material undergoes no perceptible change. In the case of active combustion, the action is crowded into a few minutes or seconds, and, as all the heat developed is evolved in this short space of time, the temperature of the substances rapidly rises to the point at which light is emitted.

That heat is developed during the process of spontaneous oxida-

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* The major calorie sometimes used is equal to 1000 calories. See Thermochemistry, Part I. chap. xv.

tion is readily shown. Thus, if a small heap of fragments of phosphorus be exposed to the air, it will be evident from the formation of fumes of oxide that it is undergoing oxidation. As the action proceeds, and as the heat produced by the oxidation is developed more rapidly than it is radiated away (especially from the interior portions of the heap), it will be seen that the phosphorus quickly begins to melt, and finally the temperature will rise to the point at which *active* combustion begins, when the mass will burst into flame.

It has been shown that many destructive fires have arisen from masses of combustible material, such as heaps of oily cotton waste, undergoing this process of spontaneous oxidation, until the heat developed within the mass has risen sufficiently high to inflame the material. To the operation of the same causes is to be referred the spontaneous firing of haystacks which have been built with damp hay, and also the spontaneous inflammation of coal in the holds of ships.

As the temperature produced by combustion is augmented by increasing the rapidity with which the chemical action takes place, it will be at once obvious why substances which burn in the air, burn with increased brilliancy and with higher temperature in pure oxygen. In the air every molecule of oxygen is surrounded by four molecules of nitrogen, therefore for every one molecule of oxygen that comes in contact with the burning substance, four molecules of this inert element strike it; and by so doing they not only prevent the contact of so much oxygen in a given interval of time, but they themselves have their temperature raised at the expense of the heat of the burning material. The number of oxygen molecules coming in contact with a substance burning in the air, in a given time, may be increased by artificially setting the air in rapid motion: hence the increased rapidity of combustion (and consequent rise of temperature) that is effected by the use of bellows, or by increasing the draught by means of chimneys and dampers.

The augmentation of temperature obtained by the substitution of pure oxygen for air is well illustrated in the case of burning hydrogen. The temperature of the flame of hydrogen burning in oxygen, known as the oxy-hydrogen flame, is extremely high, and when allowed to impinge upon a fragment of lime, it quickly raises the temperature of that substance to an intense white heat, when it emits a powerful light—the so-called *oxy-hydrogen limelight*.

The following results obtained by Bunsen show the temperatures reached by the combustion of hydrogen, and of carbon monoxide, in air and in oxygen—

The flame of hydrogen burning in air . . .	2024°
„ „ „ oxygen . .	2844°
„ carbon monoxide burning in air .	1997°
„ „ „ oxygen	3003°

It will be seen that whereas the flame of hydrogen in air is hotter than that of carbon monoxide in air, when these gases burn in oxygen the temperature of the carbon monoxide flame is higher than that of hydrogen. This is due to the partial dissociation of the water which results from the combustion of the latter. It has been shown that when a mixture of hydrogen and oxygen, in the proportion to form water, is ignited, the temperature produced by the union of a portion of the mixture rises above the point at which water dissociates; and consequently for a certain small interval of time a condition of equilibrium obtains, during which as many molecules of water are dissociated as are formed: during this state the temperature falls, when rapid combustion once more proceeds. It will be seen, therefore, that the limits to the temperature which can be reached by combustion are influenced by the points at which the products of combustion undergo dissociation.

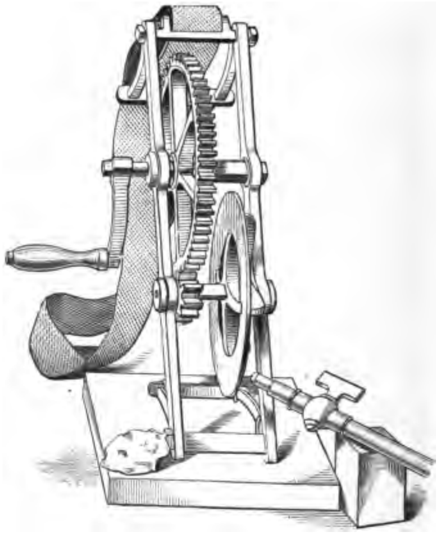

FIG. 77.

Ignition Point.—The temperature to which a substance must be raised in order that combustion may take place is called its *ignition point.* Every combustible substance has its own ignition temperature. If this point be below the ordinary temperature the substance will obviously take fire when brought into the air, without the application of heat; such substances are said to be *spontaneously inflammable*, and must necessarily be preserved out of contact with air.

Passing from cases of spontaneous inflammability, we find a very wide range existing between the igniting points of different substances. Thus, a jet of gaseous phosphoretted hydrogen may be ignited by causing it to impinge upon a test-tube containing boiling water; carbon disulphide vapour is inflamed by a glass rod heated to 120°, while the diamond requires to be raised nearly to a white heat before combustion begins.

The difference between the temperatures of ignition of hydrogen and marsh gas may be well seen by means of the old *steel mill* of the miner (Fig. 77). By causing the steel disk to revolve at a high speed, while a fragment of flint is lightly pressed against its edge, a shower of sparks is thrown out; and on directing a jet of hydrogen upon these sparks the gas is instantly ignited, while they may be projected into a stream of marsh gas without causing its inflammation. The same fact is also made strikingly apparent by depressing a piece of fine wire gauze upon flames of marsh gas (or coal gas) and hydrogen. In the former case the flame will not pass through the gauze, although it may be shown that marsh gas is making its way through by applying a lighted taper immediately above the wire. If the gauze be held over the issuing jet of gas the latter may be ignited by a taper upon the upper side of the gauze, but the combustion will not be communicated to the inflammable gas beneath (Fig. 78). The gauze conducts the heat away from the flame so rapidly that the temperature of the metal does not rise to the ignition point of the marsh gas on the other side, and therefore the combustion cannot be propagated through

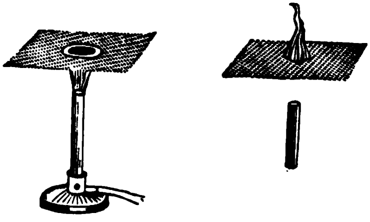

FIG. 78.

the gauze. In the case of hydrogen, however, it will be found that the instant the gas upon the upper side of the gauze is inflamed the flame passes through and ignites the hydrogen beneath.*

It is upon this principle that the safety of the "Davy lamp" depends. This consists of an ordinary oil lamp, the flame of which is surrounded by a cylinder of wire gauze (usually made double at the top), through which air to supply the flame freely passes in and the products of combustion pass out. When such a lamp is taken into an atmosphere in which marsh gas is present, this gas, entering through the gauze, becomes ignited within the chimney, producing a very characteristic effect upon the lamp flame. According to the amount of marsh gas present the flame is seen to become more and more extended, at the same time becoming less luminous, until the whole interior of the gauze cylinder is filled with the burning gas, emitting a faint bluish light, known among the miners as the *corpse-light.* The burning marsh gas is unable to communicate its combustion to the inflammable mixture outside, for the same reason that the flame, in the experiment already referred to, was unable to pass through the wire gauze. If from any cause the flame should heat any spot of the gauze chimney to a temperature above the ignition point of marsh gas, the outside combustible mixture will become ignited. It has been shown that by exposing the lamp to a strong air draught the flame may be so driven against the gauze as to unduly heat the metal. It has also been proved that the same result frequently follows from the explosive wave that is produced in a mine when, from some accidental cause, the operation of blasting (or *shot-firing*) results, not in the splitting of the rock, but in merely blowing out the "tamping." The violent concussion to the air which follows such a *blown-out shot* has been known to blow the flames of the Davy lamps, even in remote parts of the workings, bodily through the gauze; and if such lamps are burning at the time in an inflammable mixture, it would thereby be fired.

By the behaviour of the flame of a Davy lamp when placed into an atmosphere containing marsh gas, it is possible to estimate, with a rough degree of accuracy, the percentage amount of that gas which is present. For this purpose the flame is turned down as low as possible, and the height to which the burning marsh gas extends (the so-called *fire-damp cap*) is measured against a scale graduated in tenths of inches. Fig. 79 (two-thirds the actual size) shows the "caps" obtained by the presence of 4, 5, and 6 per cent. of marsh gas.†

When the ignition point of a substance is lower than the temperature produced by its combustion, such a substance, when

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* Recent experiments of Victor Meyer (*Berichte*, No. 16, 1893), upon the ignition temperature of explosive gaseous mixtures, give the following results:—

A mixture of oxygen and hydrogen (electrolytic gas) explodes at	612°
Explosive mixture of oxygen and marsh gas	656°
,, ,, ,, coal gas	647°

† In a recent development of this method of testing, a small hydrogen flame is substituted for the oil lamp flame, whereby it is possible to detect the presence of 0.25 per cent. of marsh gas (Clowes).

ignited, will continue to burn without further application of external heat, the inflammation being propagated from particle to particle by the heat developed by their own combustion. All the ordinary processes of combustion are actions of this order, and belong to the class of chemical reactions known as *exothermic*, that is to say, reactions which are accompanied by an evolution of heat (page 168).

If, on the other hand, the ignition point be higher than the heat produced by chemical union, combustion cannot proceed without the continuous application of external heat. The igniting point of nitrogen in oxygen, for example, is higher than the temperature produced by the union of these elements; therefore, although the nitrogen may be ignited by the heat of the electric spark, it is unable to communicate its combustion to contiguous particles, and the inflammation does not spread. If the ignition point of nitrogen in oxygen had been *lower* instead of *higher* than the heat of the chemical union of these elements, the first flash of lightning that discharged into the air would have initiated a conflagration, which would have extended through the whole atmosphere, and resulted in the removal of the oxygen and its replacement by oxides of nitrogen.

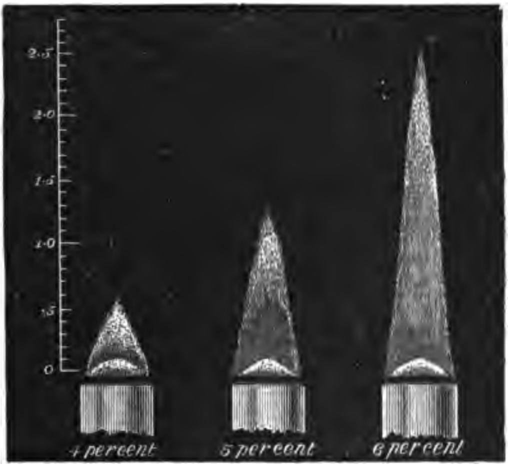

FIG. 79.

The production of acetylene by the combination of carbon with hydrogen under the influence of high temperature, and the formation of cyanogen and carbon disulphide, by the union of the same element with nitrogen and with sulphur respectively, are illustrations of the same class of action: phenomena of this order being known as *endothermic* reactions, that is, reactions that are attended with an absorption of heat (page 168).

Flame.—When both the substances taking part in combustion are gases or vapours, the sphere of the chemical action assumes the character of flame; while, on the other hand, if one of the materials is a solid which is not volatile at the temperature of its combustion, no flame accompanies its burning. Such solids as sulphur, phosphorus, camphor, wax, &c., during combustion in air, undergo vaporisation, and consequently burn with the formation of flame; while such substances as iron, copper, carbon,* &c., which do not pass into vapour at the temperature produced by their combustion in oxygen, burn in this gas without giving rise to a flame.

Flames differ very widely in their general appearance, and in the majority of cases are distinctly characteristic: thus, hydrogen burns in air with a flame that is almost absolutely colourless, and is scarcely visible in bright daylight; sulphur burning in air produces a pale blue flame; ammonia in oxygen a flame having a yellow-ochre colour; carbon monoxide a rich blue flame; while cyanogen burns with a flame having the delicate colour of the peach blossom. Other flames are characterised by their luminosity. Thus, phosphorus burning in oxygen emits a dazzling yellow light, that is almost blinding to the eyes; magnesium burns in the air with an intense bluish-white light; the flame produced by the combustion of the vapour of nickel carbonyl in air emits a bright white light; and the flames that are produced by most hydrocarbons during their combustion give a characteristic yellowish-white light.

The General Structure of Flame.—The simplest form of flame is one that is obtained by the combustion of a substance which itself undergoes no decomposition, and in which the product of combustion is arrived at in a single stage. Such flames, for example, as that of hydrogen burning in chlorine or in air, or of carbon monoxide burning in air. In the case of hydrogen burning in air, the materials taking part in the process being elementary

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* Under certain conditions the combustion of carbon in oxygen is accompanied by flame; but it has been shown that at the temperature at which this occurs carbon monoxide is being formed.

bodies, no complications arising from decomposition are possible; and although carbon monoxide is a compound, it unites with oxygen without itself undergoing any decomposition, and passes directly into carbon dioxide. Such flames as these, when burning from the end of a tube, consist of a single hollow conical sheath of actively burning gas. Fig. 80 represents a flame of burning hydrogen: the darker region *d* is the hollow space within the flame, consisting of unburnt hydrogen; while the flame proper, the actual burning portion, is the sheath *b*, which appears practically uniform throughout. That the flame-cone is hollow may be proved by a variety of experiments. Thus, if a sheet of white paper be quickly depressed into a flame, a charred impression of the section of the cone will be obtained, as shown in Fig. 81, from which it will be seen that no combustion is taking place within the cone. In the same way, an ordinary lucifer match may be suspended within the flame, where it will remain without ignition so long as the burning walls of the flame do not touch it. The shape of a flame is due to the fact, that as the gas issues, the layer nearest to the walls of the tube burn round the orifice of the tube as a ring, consequently the next layer has to reach up above this ring before it can meet with air for its combustion, and each successive layer has to pass up higher and higher in order to find its supply of air, and in this way the burning area is built up into the form of a cone. To show that the hollow space consists of unburnt gas, it is only necessary to insert a tube into the interior of the flame in such a way as to

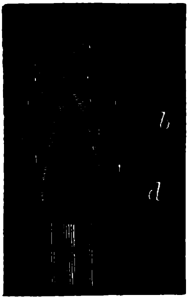

FIG. 80.

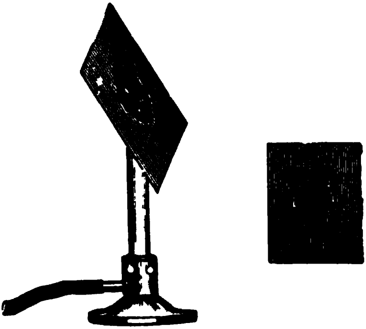

FIG. 81.

draw off a portion of the gas, when it will be found that the gas so withdrawn will burn.

Passing from this simplest type to substances that undergo decomposition during combustion, or which yield the final product of oxidation by successive stages, it is found that the flames they give rise to are less simple in structure.

As illustrations of various degrees of complexity, the following examples may be mentioned :—

(1.) Ammonia burning in oxygen. This flame (Fig. 82) is very characteristic, and on inspection it is at once obvious that it has a less simple structure than the hydrogen flame. In this case the inner hollow portion *d* is surrounded by a double flame-cone, the inner cone *a* having a yellow-ochre colour, and the outer portion *b* possessing a much paler colour, and tending to green. During the combustion of ammonia, the compound undergoes decomposition into nitrogen and hydrogen. This decomposition, which begins in the hollow region *d*, takes place mainly in the inner cone *a*, and the hydrogen which escapes combustion in this region passes to the outside, and there burns, forming the outer cone. Probably there is also a partial combustion of the nitrogen.

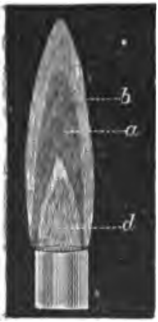

FIG. 82.

(2.) Carbon disulphide burning in air. This flame, like the ammonia flame, consists of a double flame-cone, consisting of an inner lilac-coloured cone, surrounded by an outer region having a deeper blue colour. During combustion carbon disulphide, like ammonia, is decomposed, but in this case not only are *both* of the constituents readily combustible, but the carbon passes into its final state of oxidation in two stages, forming first carbon monoxide and afterwards carbon dioxide.

(3.) Hydrocarbons burning in air. The flames produced by the combustion of these compounds include those which are commonly employed for illuminating purposes, such as candle, gas, and oil flames, and in all essential points of construction they are practically identical.. This may be seen to be the case by a comparison of the flames of a candle and of coal gas (Figs. 83 and 84). In these flames, as in the former cases, there is the dark hollow space *d*, consisting of heated unburnt gas (in the candle flame this gas is generated by the vaporisation of the materials of the candle, which in the melted condition are drawn up the wick by capillary action). Above this there is a region, *a*, which, in comparison with the rest of the flame, appears almost opaque, and which emits a bright yellow light. This luminous area constitutes relatively the largest part of the flame, and in flames that are used for light-giving purposes it is intentionally made as large as possible by means of various devices. At the base of the flame there is a small region, *c*, which appears bright blue in colour, and is non-luminous; and surrounding the entire flame there will be seen a faintly luminous mantle, *b*.

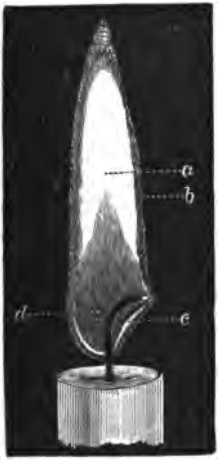

FIG. 83.

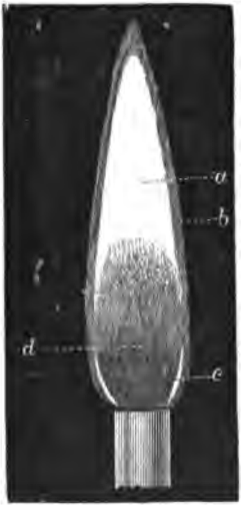

FIG. 84.

The flame proper, therefore, consists of three distinct parts, namely: (1) the blue region *c*, at the base; (2) the faintly luminous mantle *b*; and (3) the yellow, brightly luminous region *a*. These three parts constitute the flame-cone, the actual area of combustion, which envelops the dark region *d*; this, as already stated, consists of unburnt gas, and therefore is not, strictly speaking, a part of the flame.

If the supply of gas to a flame, burning as represented in Fig. 84, be diminished, or if air be slowly admitted to the interior, the flame will shrink down, and the luminous area become less and less, until it finally disappears altogether. The flame-cone will then be found to consist of two parts, resembling in structure the double cone of the ammonia flame, Fig. 82. The blue region *c*, Fig. 84, which is only fragmentary in the flame as there represented, will have become continuous, and now constitutes the inner cone; while the mantle *b* forms the outer cone, the flame presenting the appearance seen in Fig. 85. The region *d*, as before, consists of unburnt gas.

It has been shown, in the case of coal gas flames burning in this manner, that in the inner cone *c*, the changes going on result mainly in the formation of carbon monoxide and water, together with small quantities of carbon dioxide and hydrogen; and that in the outer cone, or mantle, the carbon monoxide and hydrogen are burning to carbon dioxide and water. In the inner cone, therefore, the carbon is burnt to its first stage of oxidation, and a portion of the hydrogen is oxidised to water; in the outer cone, the second stage of oxidation of the carbon takes place by the combustion of the carbon monoxide to carbon dioxide, and the hydrogen which escapes combustion in the inner cone is also burnt.

FIG. 85.

It has been known since the time of Dalton, that when certain hydrocarbons are burnt with an insufficient amount of oxygen for the complete oxidation of both the hydrogen and carbon, carbon monoxide, water, and hydrogen are produced. This result is probably due to a secondary reaction; the first stage being the combustion of hydrogen to form water, which at the high temperature is then decomposed, either by the carbon or the hydrocarbons, according to the following equations—

$$CH_4 + O_2 = 2H_2O + C = CO + H_2 + H_2O.$$
$$C_2H_4 + O_2 = 2H_2O + 2C = 2CO + 2H_2.$$

The various parts of an ordinary gas or candle flame, therefore, are due to the different chemical reactions that are taking place in these areas; these changes are not of such a nature that they can in all cases be perfectly traced, neither is one set of reactions exclusively confined to each area, but rather is it the case that certain chemical actions predominate in each particular part of the flame.

In the blue region *c*, Figs. 83 and 84, the main reactions going forward are those already indicated, by which carbon monoxide, water, and hydrogen are produced. In the faintly luminous mantle *b*, carbon monoxide and hydrogen are burning, together with small quantities of hydrocarbons which may have escaped combustion and decomposition in the luminous region. The non-luminous character of this mantle is due to the cooling effect of the air which is drawn into the flame, and which even extinguishes combustion upon the outer limits of the flame before every trace of combustible material is burnt; for it has been shown that small quantities of carbon monoxide, marsh gas, and even hydrogen escape unburnt from a gas flame.

The chemical decompositions which go on in the luminous area cannot be said to have been thoroughly established. It has been shown that very early in its passage up the flame a certain amount of the marsh gas and ethylene present is converted into acetylene, the change taking place as the result of heat alone. The gases ascending the dark region *d* are surrounded on all sides by a wall of burning material, and are thereby raised in temperature to the point at which the marsh gas and ethylene suffer decomposition into acetylene and hydrogen—

$$2CH_4 = C_2H_2 + 3H_2.$$

The following table (Lewes) shows the gradual development of acetylene in such a flame :—

	Total Unsaturated Hydrocarbons. Per Cent.	Acetylene. Per Cent.
Gas in burner	4.38	0.035
½ inch above rim of burner . .	4.00	0.340
1½ inch above rim . . .	1.53	0.560
Tip of dark region . . .	1.98	1.410
Centre of luminous area . .	0.45	0.045
Tip of luminous area . . .	0.00	0.00

Therefore, by the time the gases have reached the tip of the dark region, the effect of heat upon them has been to raise the amount of acetylene to over 70 per cent. of the total unsaturated hydrocarbons present. As the acetylene and other hydrocarbons pass on through the flame along with steam, carbon dioxide, and carbon monoxide, other and more complex changes go on whereby denser hydrocarbons are formed, and carbon itself is precipitated.

The formation of acetylene in that region of the flame where the coal gas is in excess is well exemplified in the case of air burning in an atmosphere of coal gas (see Fig. 75). In this flame the air is in the inside and the coal gas upon the outside; it is, in effect, an ordinary coal gas flame *turned inside out*. The formation of acetylene, instead of taking place *within* the flame (in which case it has to pass through the heated area and is thereby decomposed), takes place upon the outer surface or periphery of the flame, and therefore largely escapes combustion and decomposition and passes away into the coal gas atmosphere. (See Acetylene, where this method is described for the preparation of this compound.)

The Cause of Luminosity in Flames.—The light-giving property of a flame is not due to the operation of any one simple cause. It was at one time supposed that the luminosity of a flame depended solely upon the presence *in it* of suspended solid matter resulting from the chemical decompositions going on during combustion. It has been shown, however, that this general statement does not satisfy all cases, as there are a number of highly luminous flames in which, from the known properties of the products of combustion, there cannot possibly be any solid matter present. Thus, for example, phosphorus burning in air gives a flame of a high degree of luminosity; but the phosphorus pentoxide which is the product of combustion, although solid at ordinary temperatures, is volatile at a temperature far below that of the flame. The same may be said of the luminous flame of arsenic burning in oxygen, where the still more volatile arsenious oxide is the product.

When carbon disulphide burns in oxygen or in nitric oxide, a well-known and intensely luminous flame is obtained, in which only gaseous products of combustion can be present; and, lastly, the flame of hydrogen burning in oxygen can be made under certain circumstances to emit a bright light: thus, when a mixture of these gases is ignited in a closed eudiometer, their combustion is attended with a brilliant flash of light, the only product being water.

There are three causes which may operate, either separately or together, in imparting luminosity to a flame or in increasing its light-giving power: these are—(1.) The temperature of the flame; (2.) the density of the flame gases; and (3.) the introduction into the flame of solid matter. These three causes will be treated separately and illustrations given, which, so far as our knowledge extends, can be directly traced to the independent operation of each.

(1.) The effect of temperature.

(*a*.) Upon flames in which solid matter is known to be absent.

When phosphorus is introduced into chlorine, it spontaneously inflames and burns with a flame of such extremely feeble luminosity that it may be regarded as non-luminous; if, however, the chlorine be previously strongly heated by being passed through a red-hot tube, and the phosphorus be boiling when it comes in contact with the gas, the combustion thus started upon a higher platform of temperature is accompanied by a flame of very considerable luminosity.

The flame of carbon disulphide burning in air emits but a feeble light; but when this substance burns in pure oxygen, its temperature of combustion is greatly raised and the luminosity of the flame is enormously increased.

Phosphoretted hydrogen burning in air gives a flame of considerable luminosity; but when this flame is fed with pure oxygen, and its temperature thereby raised, it becomes intensely luminous.

(β.) Upon flames in which solid matter is known to be present.

The flames produced by the combustion of zinc or magnesium in the air, and in which the solid oxides are present, have their luminosity greatly increased when pure oxygen is substituted for air and the temperature of combustion thereby augmented.

The same result is seen in the case of flames in which the solid matter is artificially introduced, as in the familiar Welsbach burner, where a solid gauze mantle, composed of an alkaline earth, is placed in the flame-cone of a non-luminous gas flame, thereby rendering it luminous. If the temperature of this flame be augmented by feeding it with oxygen, the light emitted by the incandescent solid is greatly increased.

(γ.) Upon flames in which solid matter is believed to be present, such as candle, gas, and other hydrocarbon flames.

When a candle or gas flame is introduced into oxygen, although it shrinks in size, its luminosity is increased. It has also been shown that when a coal gas flame is chilled by causing it to spread against a cold surface, its luminosity is diminished or destroyed altogether; and, conversely, if the gas and the air supplying the flame be strongly heated before combustion, the luminosity is greatly increased. In this case, however, the direct effect of change of temperature is complicated by the decompositions going on in the flame; for, as already mentioned, the conversion of the non-illuminating marsh gas into the highly illuminating gas acetylene is a function of the temperature.

The increase of light obtained from a gas flame by previously heating the gas and air is the principle underlying all the so-called *recuperative* burners.

It is evident, therefore, that most flames gain luminosity by having their temperature raised. There are, however, cases in which increase of temperature *alone* appears to exert no influence upon the luminosity. The flame of hydrogen, for example, which is practically non-luminous when burning in air, does not become more luminous when burnt in oxygen, although its temperature is greatly increased.

(2.) The influence of the density of the flame gases.

It has been shown by Frankland * that the luminosity of flame is intimately associated with the pressure to which it is subjected, or with the density of the flame gases. Thus, it is found that a gas or candle flame, when burnt either at high altitudes or in artificially rarefied atmospheres, has its luminosity greatly reduced ; and, *per contra*, when caused to burn under increased pressure, the luminosity is increased. In the case of hydrocarbons, complication arises from the fact that the temperature of the flame is changed by alterations

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* *Phil. Trans.*, vol. cli. p. 629; *Proc. Royal Society*, vol. xvi. p. 419.

of pressure. Under diminished pressure the temperature falls, and although there is less loss of heat by radiation in rarefied air than in air at the ordinary pressure, it is possible that the general lowering of the temperature of the flame may modify the chemical decompositions in the direction already referred to.

Flames other than those of hydrocarbons, however, and in which no solid matter can exist, are found to become luminous when the density of the flame gas is increased by pressure. Thus, the flame of carbon monoxide in oxygen at ordinary pressures emits a moderate light; but when exposed to a pressure of two atmospheres the luminosity is greatly increased. Even the non-luminous flame of hydrogen burning in oxygen becomes luminous under a pressure of two atmospheres, and when examined by the spectroscope is found to give a continuous spectrum. It has been found, as a general rule, that dense gases and vapours, when heated, become incandescent or luminous at much lower temperatures than those of low specific gravity; thus, if different gases be raised to incandescence by the passage through them of electric sparks, under similar conditions, it is seen that the light emitted by the glowing vapour varies with the density of the gas. The luminosity of glowing oxygen (density, 16) is greatly superior to that of hydrogen (density, 1), while the light emitted when the sparks are passed through chlorine (density, 35.5) is considerably in advance of either. And it is found that in one and the same gas the luminosity of the spark increases as the density is increased by artificial compression. Other things being equal, it may be said that the denser the vapours which are present the more luminous is the flame.

FIG. 86.

FIG. 87.

(3.) The introduction of solid matter into flames.

Non-luminous flames may be rendered luminous by the intentional introduction into them of solid matter, which, by being raised to a sufficiently high temperature, will become strongly incandescent. Thus, the ordinary lime-light owes its luminosity to the incandescence of the fragment of lime, which is raised to a bright white heat by the high temperature of the non-luminous oxy-hydrogen flame. The lime is not vaporised at the temperature of the flame, the light being entirely due to the glowing solid matter.

The "Welsbach" burner, already referred to, is another example of the same order, the luminosity in this case being due to the introduction into an ordinary non-luminous Bunsen flame of a fine gauze mantle made of thoria or other metallic oxide (Fig. 86). When such a mantle is raised to incandescence by the heat of the gas flame, it emits a bright white light, strongly resembling that of an ordinary Argand gas flame. A flame may also be rendered luminous by the intentional precipitation within it of carbon, which, by its ignition and its combustion, produces a high degree of luminosity. Thus, if a small quantity of alcohol be boiled in a flask, and a jet from which chlorine is issuing be then lowered through the burning vapour into the flask, as shown in Fig. 87, the chlorine will burn in the alcohol vapour with a luminous flame; and the precipitated carbon (which is thrown out of combination by the action of the chlorine upon the alcohol), ascending into the previously non-luminous alcohol flame, will render it brightly luminous.

From these considerations it will be evident that the luminosity of a flame may be due, first, to the presence of vapours sufficiently dense to become incandescent at the temperature of the flame; or, second, to the presence of solids rendered incandescent, either by the heat of the flame gases alone, or in conjunction with their own combustion; or, third, from the simultaneous operation of all these causes. Ordinary gas and candle flames come under the last of these heads. The decompositions that go forward in these flames not only give rise to dense vapours which become incandescent, but also to the precipitation of solid carbon, which by its ignition and combustion adds to the luminosity of the flame.

The Bunsen Flame.—The construction of the Bunsen lamp is too well known to need description. The gas, issuing from a small jet situated at the base of a metal tube, and mixing with air which is drawn in through openings in the tube, burns at the top of the chimney with the familiar non-luminous flame. The existence of this flame in its ordinary condition depends upon two main causes; first, upon the fact that in the immediate neighbourhood of a jet of gas issuing from a small orifice, there is a reduction of pressure; and, second, upon the relation between the velocity at which the gases pass up the tube and the rate of propagation of combustion in the mixture of air and coal gas. Upon the first of these causes depends the entrance of air into the "air-holes" of the lamp, and upon the second depends the continuance of the flame in its position upon the top of the tube.

As the coal gas issues from the small jet at the base of the chimney, instead of the gas escaping through the side-holes, air is drawn into the tube by virtue of the reduced pressure produced immediately round the jet. That this area of reduced pressure actually exists in the neighbourhood of the jet of a Bunsen may be proved by attaching a delicate manometer to the air-hole of such a lamp, as shown in Fig. 88. As the gas is turned on, the liquid in the horizontal tube will be sucked towards the lamp, showing that the issuing gas causes a partial vacuum in its immediate neighbourhood.*

In order that the flame shall remain at the top of the tube, there must be a certain relation between the velocity of the issuing gases and the rate of propagation of combustion in the mixture; for if the latter be greater than the former, the flame will travel down the tube and ignite the gas at the jet below. By gradually reducing the supply of gas to the flame, and so altering the proportion of gas and air ascending the tube, the mixture becomes more and more explosive, until a point is reached when the velocity of inflammation is greater than the rate of efflux of the gases, and the flame travels down the tube, and the familiar effect of the flame "striking down" is obtained.

The same result may be brought about, and the effect more closely observed, by extending the chimney of the lamp by means of a wide glass tube. As the supply of gas is reduced, or the quantity of air introduced is increased, the flame will be seen to shrink in size and finally descend the tube. By adjustment it may be caused either to explode rapidly down the tube or to travel quite slowly, or even to remain stationary at some point in the tube, which is slightly constricted, and where, therefore, the flow of the issuing gas is slightly accelerated.†

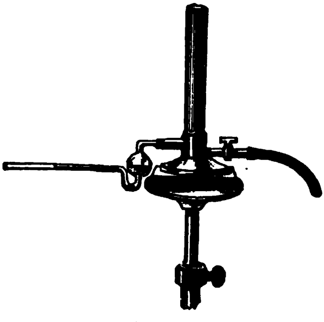

FIG. 88.

The non-luminosity of a Bunsen flame is due to the combined operation of three causes, namely, oxidation, dilution, and cooling. It was formerly supposed that the destruction of the luminosity of a gas flame by the admixture of air with the gas before burning was entirely owing to the influence of the oxygen in bringing about a more rapid and complete state of oxidation, that the hydrocarbons were at once completely burnt up by the additional supply of oxygen so provided. It has been shown, however, that not only is this effect brought about by air, but also by the use of such inert gases as nitrogen, carbon dioxide, and even steam. The following table (Lewes) shows the relative volumes of various gases that are required to destroy the luminosity of a gas flame:—

1 volume	of coal gas	requires	0.5	volumes of	oxygen.
,,	,,	,,	1.26	,,	carbon dioxide.
,,	,,	,,	2.27	,,	air.
,,	,,	,,	2.30	,,	nitrogen.
,,	,,	,,	5.11	,,	carbon monoxide.

That the atmospheric oxygen effects the result by a direct oxidising action, and is not acting merely as nitrogen does, is proved by the fact that mixtures of oxygen and nitrogen, containing a higher proportion of oxygen than is

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* See "Chemical Lecture Experiments," new ed., 498–502. † Ibid., 506.

present in air, destroy the luminosity more rapidly than is effected by air. Thus, when mixtures containing nitrogen and oxygen in the proportion of 3 to 1, 2 to 1, 1 to 1 by volume are employed, the volumes of the mixtures required to destroy the luminosity of one volume of coal gas are respectively 2.02, 1.49, and 1.00.

It has been shown that when coal gas is diluted with nitrogen a higher temperature is necessary to effect its decomposition; hence the action of the atmospheric nitrogen in causing the loss of luminosity of a gas flame is in part due to the higher temperature that is required for the formation of acetylene, which, as already mentioned, is the first step in the decomposition and condensation of the hydrocarbons in the gas.

As already mentioned, the luminosity of a flame is very much influenced by alterations of temperature; and just as the non-luminosity of the outer mantle of an ordinary flame is partly due to the cooling action of the air which is dragged into the flame from the outside, so the want of luminosity of the Bunsen flame is in part due to the cooling influence of the large volume of air that is drawn up into the interior of the flame. That the gases which are drawn into a flame reduce the luminosity by virtue of their cooling action is borne out by the fact that the higher the specific heat of the diluent (and therefore the greater its power to abstract heat from the flame) the less of it is required to effect the destruction of the luminosity; thus, as already mentioned, less carbon dioxide than nitrogen is necessary to render a flame non-luminous: the specific heat of nitrogen is 0.2370, while that of carbon dioxide is 0.3307.

The specific heat of oxygen is also slightly greater than that of nitrogen, being 0.2405; but the cooling effect of dilution with this gas is enormously overpowered by the increased temperature due to its oxidising action upon the combustible materials of the flame.

Experiments made upon the actual temperatures of various regions of a Bunsen flame, rendered non-luminous by admixture with different gases, the results of which are seen in the following table (Lewes), show the cooling effect of these diluents upon the flame:—

Temperature of Flame from Bunsen Burner, burning 6 *cubic feet of Coal Gas per Hour.*

Region in Flame.	Luminous Flame.	Flame rendered Non-luminous by		
		Air.	Nitrogen.	Carbon Dioxide.
	Degrees.	Degrees.	Degrees.	Degrees.
½ inch above burner	135	54	30	35
1½ inch above burner	421	175	111	70
Tip of inner cone	913	1090	444	393
Centre of outer cone	1328	1533	999	770
Tip of outer cone	728	1175	1151	951
Side of outer cone, level with tip of inner cone	1236	1333	1236	970

In the case of air, it will be seen that the first effect is to cool the flame; but in the upper region, where the oxidising action of the oxygen is felt, the temperature rapidly rises to a maximum at a point about half-way between the tip of the inner and outer cones. In the flames rendered non-luminous by the two inert gases, the highest temperature is only reached at the outer limit, where the full amount of oxygen for combustion is obtained from the outer atmosphere.

On account of the wide range of temperature exhibited by the various regions of a Bunsen flame, it constitutes a most valuable analytical instrument, for, by the judicious use of the different parts of the flame, it is often possible to detect the presence of several flame-colouring substances in a mixture. Thus, if a mixture of sodium and potassium salts be introduced upon platinum wire into the cooler region of the flame near its base, the more volatile potassium compound will impart its characteristic violet tint to the flame before the sodium salt is volatilised sufficiently to mask the colour, by the strong yellow it itself gives to the flame. In this way many mixtures may readily be differentiated.

If a piece of copper wire be held horizontally across a Bunsen flame, so as to cut the inner cone, it will be seen that the wire in contact with the edges of the flame becomes coated with copper oxide, while the portion in the centre remains bright. On moving the wire so as to bring the oxidised portion into the inner region, the oxide will be reduced, the metal once more becoming bright. The outer area of a flame, where oxygen is in excess, is called the *oxidising flame;* while the inner region, in which heated and unburnt hydrogen or hydrocarbons exist, is spoken of as the *reducing flame.* These regions exist in all ordinary flames. The oxidising action of the outer flame of a candle, for example, is illustrated in the behaviour of the wick. So long as the wick remains in the inner region of the flame it is not burnt; and in the early days of candles, as the tallow gradually consumed, the wick remained standing straight up, and by degrees extended into the luminous area of the flame, where, owing to the deposition of soot upon it, it frequently developed a cauliflower-like accretion, which greatly impaired the luminosity of the flame, and which necessitated the use of snuffers. In the modern candle, owing to a method of plaiting the wick, it is caused to bend over (as shown in Fig. 83), and so thrusts its point into the oxidising region, where it is continually burnt away.