Advanced inorganic chemistry / by G.H. Bailey ; edited by William Briggs.

ADVANCED
INORGANIC CHEMISTRY

Edw^{d} A Grieg

The Organized Science Series.

General Editor: WILLIAM BRIGGS, M.A., LL.B., F.C.S., F.R.A.S.

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PREFACE.

THIS book is specially adapted to the requirements of the syllabus of the Advanced Stage Inorganic Chemistry issued by the Science and Art Department.

It is assumed that the student has already worked through the Elementary Stage and acquired a general knowledge of the chemistry of the Non-metals; hence in this section only matter of a supplementary character is given.

The subject of Chemical Physics as well as the chemical operations employed on the manufacturing scale have both been dealt with at greater length than is usual in a work of such moderate dimensions.

The importance attached in the syllabus to these branches fully justifies this liberality of treatment.

The metals and their chief compounds have been considered in the order suggested by the periodic system, and prefixed to each group a summary of the chief characteristic properties of the group will be found; it is hoped that this arrangement will enable the student to grasp most readily the principal facts relating to the metallic elements.

Another volume of this series is in preparation which will contain a course of practical work for the advanced student, but as it is believed that a thorough grasp of the subject of Chemistry can be gained only by the student performing the operations himself, an appendix appears in this work giving a list of experiments that should be performed in illustration of the subject of each chapter.

November, 1898.

CONTENTS.

APPENDICES.

The Chemical Elements.

Arranged according to the Periodic System.

GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.		
Hydrogen, H. 1									
Lithium, Li. 7	Beryllium, Be. 9·1	Boron, B. 10·9	Carbon, C. 12	Nitrogen, N. 14	Oxygen, O. 16	Fluorine, F. 19			
Sodium, Na. 23	Magnesium, Mg. 24	Aluminium, Al. 27	Silicon, Si. 28	Phosphorus, P. 31	Sulphur, S. 32	Chlorine, Cl. 35·4			
Potassium, K. 39	Calcium, Ca. 40	Scandium, Sc. 44	Titanium, Ti. 48	Vanadium, V. 51	Chromium, Cr. 52·5	Manganese, Mn. 54·8	Iron, Fe. 56	Cobalt, Co. 58.6	Nickel, Ni. 58·6
Copper Cu. 63·2	Zinc, Zn. 65·1	Gallium, Ga. 69·9	Germanium, Ge. 72·3	Arsenic, As. 75	Selenium, Se. 78·9	Bromine, Br. 79·8			
Rubidium Rb. 85·2	Strontium, Sr. 87·3	Yttrium, Y. 89	Zirconium, Zr. 90·4	Niobium, Nb. 94	Molybdenum, Mo. 96		Ruthenium, Ru. 103·5	Rhodium, Rh. 104·1	Palladium, Pd. 105·5
Silver Ag. 107·7	Cadmium Cd. 111·7	Indium, In. 113·6	Tin, Sn. 118·8	Antimony, Sb. 120	Tellurium, Te. 125	Iodine, I. 126·5			
Caesium Cs. 132·7	Barium, Ba. 136·9	Lanthanium La. 138	Cerium, Ce. 140						
		Ytterbium, Yb. 172·6		Tantalum, Ta. 182	Tungsten, W. 183·6		Osmium, Os. 191	Iridium, Ir. 192·5	Platinum, Pt. 194·3
Gold Au. 196·7	Mercury, Hg. 199·8	Thallium, Tl. 203.7	Lead, Pb. 206·4	Bismuth, Bi. 207.3					
			Thorium, Th. 232		Uranium, U. 239				

ADVANCED INORGANIC CHEMISTRY.

CHAPTER I.

PROPERTIES OF GASES.

ALTHOUGH some of the earlier philosophers regarded air as a fluid, it was not till the seventeenth century that any definite proof of this was given. Nor was it till late in the eighteenth century that (with the exception of air, hydrogen and carbon dioxide) gases were distinguished from one another as different chemical substances. At the present day, and especially amongst the non-metals and their compounds, we are acquainted with a large number of bodies which exist under ordinary atmospheric conditions in the form of gas.

The examination of the properties of gases, and of the part which they play in chemical reaction, cannot be carried out without a knowledge of their physical properties.

We purpose then to show how the weight of a gas may be determined, having regard to the allowances to be made for temperature and pressure.

The General Property of Weight of Gases.

This may be shown by suspending two similar beakers of about 5 litres content, one of them in an inverted position, at the ends of the arms of a rough balance and counterpoising them. If now hydrogen is passed into the inverted beaker by means of a tube held as far up the beaker as possible, but without coming into contact with it, and gradually lowering the tube towards the mouth of the beaker. The hydrogen will accumulate in the upper part of the beaker and gradually fill it to the mouth, pressing out the air before it. The arm of the balance will at the same time be deflected, and the beaker in question will rise. Small weights should now be added till the arm becomes horizontal again. If the beakers are of the size prescribed above, about 6 grammes will be necessary for this. If we continue to pass the gas after this, the equilibrium of the balance will not be disturbed, but on withdrawing the tube the arm bearing the inverted beaker will soon begin to fall again, showing that it is now gaining weight. This is due to the diffusion of the hydrogen out of the beaker and its replacement by air, and it will be seen how gradual such a process is.

We have seen then by this rough experiment that when 5 litres of air are replaced by 5 litres of hydrogen, a loss of weight occurs equal to about 6 grammes, which represents that a litre of hydrogren is approximately 1·2 grammes *lighter* than a litre of air.

When the whole of the hydrogen has been cleared out of the inverted beaker and replaced by air, pass carbon dioxide downwards into the other beaker, and note that it is depressed, showing that whilst hydrogen is much *lighter* than air, carbon dioxide is *heavier* than air. The weight required to restore equilibrium in this case will be found to be approximately 3 grammes.

To determine the weight of gases more accurately; suspend from the arms of a delicate chemical balance two globes fitted with stop-cocks, and having a content of about 500 c.c. In order to eliminate corrections for buoyancy of the air the two globes should be as nearly as possible similar.

Exhaust one of the globes carefully at the air-pump, and then close the stop-cock. Now attach it at one arm of the balance, and the other globe filled with dry air at the other arm, and note the weight to be added in order to bring it into equipoise. This will be the weight of 500 c.c. of air, say 0·618 gramme at the temperature and pressure prevailing at the time, say 9° C. and 750 m.m. pressure. Now attach the vacuous globe to a supply of dry hydrogen and again equipoise.

Instead of 0·618 gramme we find only 0·575, and we have the data necessary to determine—

(1) The relative density of hydrogen and air.

(2) The weight of a litre of hydrogen or air.

For the present we only know that one litre of air and of hydrogen at 90° C. and 750 m.m. pressure weigh respectively 1·236 grammes and 0·086 gramme.

We shall now consider the effect of temperature and of pressure on the volume and density of a gas.

Relation of Volume of Gases to Temperature.—Take one of the globes previously mentioned, and plunge it (with the stop-cock open) in a bath of water cooled down to 0° C. by the addition of fragments of ice. When it has remained some minutes, and the air in it has been reduced to zero, close the stop-cock and carefully dry the outside of the globe. The other globe is to be heated to 100° C. by steam or boiling water, the stop-cock is then closed, and the globe dried. Attach both to the balance, and the latter will be found to be considerably lighter than the other. The air in the globe owing to expansion has been partly expelled from the globe.

The expansion which a gas undergoes is a constant, and independent of the chemical composition of the gas. Dalton found *the expansion to be* $\frac{1}{273}$ *part of its volume at* 0° *for each increment of* 1° *C. in temperature.*

This is, however, more usually known as the Law of Charles. Stated in another form we have—

273 vols. of gas at 0° C. become 274 vols. at 1° C.
" " " 275 " " 2° C.
" " " 276 " " 3° C., and so on;
also " " " 272 " " − 1° C.
" " " 271 " " − 2° C.
" " " 270 " " − 3° C.

Now the *absolute zero* of temperature is − 273° C., and converting the temperatures stated above into degrees absolute by the addition of 273, we see that the volume of the gas will be—

At 270° absolute, 270 volumes
" 271° " 271 "
" 272° " 272 "
" 273° " 273 " &c.,

that is, the volume of a gas is *directly proportional to its absolute temperature.*

Relation of volume of Gases to the pressure to which they are subjected.—An experimental investigation of this may be made by using the simple apparatus here described. A B C is a bent glass tube of even diameter, one limb of which is made at least 8 feet long, and the other, provided with a tap at the extremity, is 40 inches. A side tube is provided at B, for running off mercury from the longer limb. It is not necessary to graduate the tubes throughout, but the following points may be marked on the shorter limb—

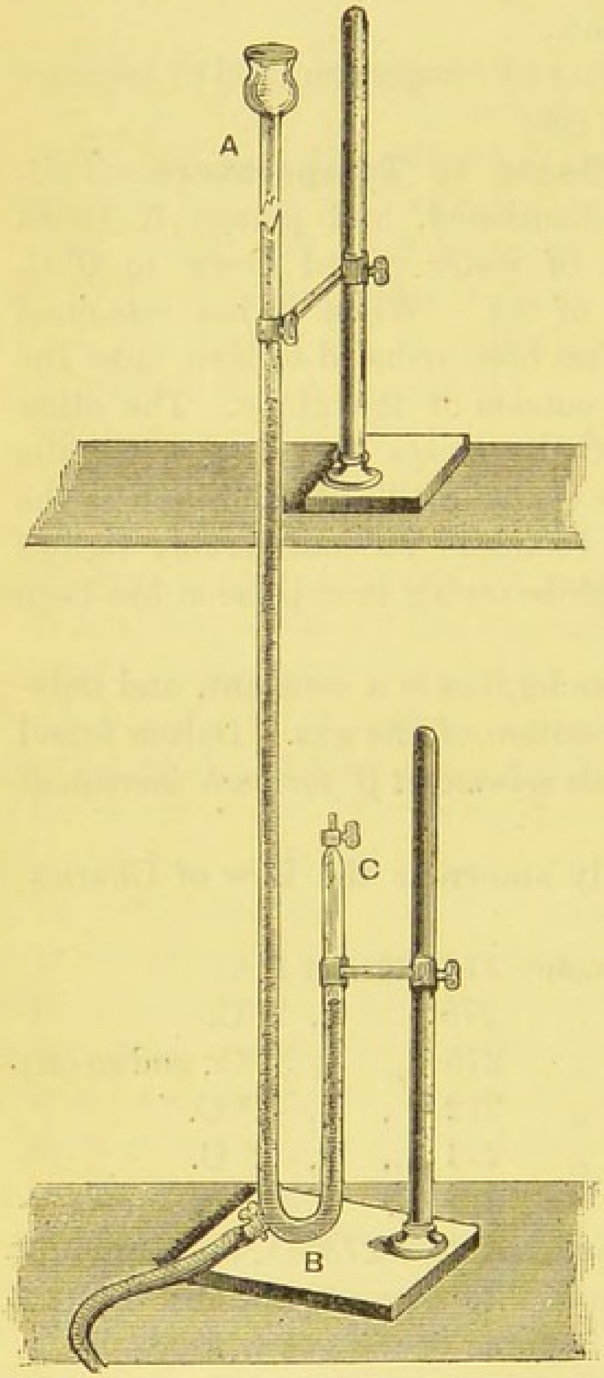

Fig. 1.

(1) a point 4 inches from C.
(2) a point 6 inches from C.
(3) a point 12 inches from C.
(4) a point 24 inches from C.
(5) a point 39 inches from C.

And on the longer limb—

(6) a point 63 inches higher than the level of (5).
(7) a point 95 inches higher than the level of (5).

Open the tap and pour in mercury to the level (3), then close the tap, and allow mercury to run off till it falls to level of (4). The pressure to which the gas is subjected is now that of the atmosphere (say 30 inches of mercury, minus the column of mercury in the shorter limb that stands above the point (5), *i. e.* 15 inches of mercury). The length of the tube occupied by the gas is now 24 inches instead of 12 inches at the outset. The pressure on the gas originally to that exerted now is in the ratio 30 : 15, or 2 : 1, and the volume of the gas (the tube being of even diameter throughout) is in the ratio 12 : 24, or 1 : 2.

Now pour in mercury till it reaches the level of (6) in the longer limb, and we shall find that in the shorter limb it will then stand at level (2). The length of the tube occupied by the gas is now 6 inches, or the volume is in the ratio 1 : 2 of that which it originally occupied. The pressure is 60 : 30, or 2 : 1.

Finally pour in more mercury till the level (7) is reached in the longer limb, and we find that in the shorter limb it will stand at level (1). The length of the tube occupied by the gas is now 4 inches, or the volume is in the ratio 1 : 3 of that which it originally occupied. The pressure is 90 : 30, or 3 : 1.

That is, placing the respective ratios of pressures and volumes side by side we have—

Pressure increased, 1 : 2.	Volume decreases, 2 : 1
„ decreased, 2 : 1.	„ increases, 1 : 2
„ „ 3 : 1.	„ „ 1 : 3,

or *when the temperature remains constant the volume occupied by a gas is inversely as the pressure.* This is known as the law of Boyle from the fact that he first gave definite experimental proof of its truth in 1662. In France and Germany it is often called Mariotte's Law, Mariotte being credited with the independent discovery of the law fourteen years later than Boyle.

It may be expressed shortly by the formula—

$$P.\ V = \text{a constant.}$$

P being the pressure, and V the volume occupied by the gas under that pressure.

If the volume is taken as unity under a pressure of 1 atmosphere, the law may be stated thus—

$$P.\ V = 1.$$

The above description is only true for a perfect gas under moderate pressure and temperature. No perfect gas exists in reality: hydrogen, nitrogen, and a few other gases behave at ordinary temperatures and pressures nearly like a perfect gas, but at very low temperatures or high pressures even these no longer agree strictly with the laws as stated. It is found indeed that all gases when placed under certain extreme conditions of temperature and pressure, behave abnormally, and ultimately pass into the liquid state, and it is only when they are far removed from this liquid state (*i. e.* at temperatures and pressures such that they are far above the boiling-point of the liquid) that they obey Charles' and Boyle's laws.

Liquefaction of gases.—By a combination of high pressure and low temperature every gas can be liquefied.

The following table gives the temperatures and pressures at which some of the commoner gases become liquids—

Carbon dioxide at	− 80° C.	and	1	atmosphere pressure.
or at	− 20° C.	,,	23	,, ,,
or at	+ 20° C.	,,	58	,, ,,
Sulphur dioxide at	− 10° C.	,,	1	,, ,,
or at	+ 10° C.	,,	2·3	,, ,,
or at	+ 30° C.	,,	5·3	,, ,,
Nitrogen at	− 193° C.	and	1	atmosphere pressure
or at	− 160° C.	,,	14	,, ,,
or at	− 146° C.	,,	52	,, ,,
Air at	− 191° C.	,,	1	,, ,,
or at	− 140° C.	,,	39	,, ,,
Ethylene at	− 103° C.	,,	1	,, ,,

A gas cannot always be liquefied by pressure alone. There is in fact a temperature peculiar to every gas *above* which the gas cannot be liquefied by any pressure whatever. Thus Andrews has shown that at temperatures above 31° C. it was impossible to liquefy carbon dioxide by pressure.

This temperature is called the *critical temperature* of the gas, so that the critical temperature of carbon dioxide is 31° C. The pressure which a gas exerts at its critical temperature is called the *critical pressure.* The following table gives these two constants for a number of gases—

	Critical temperature.	Critical pressure.
Nitrogen	− 146° C.	33 atmospheres.
Oxygen	− 119° C.	50 ,,
Nitric oxide	− 93° C.	71 ,,
Marsh gas	− 100° C.	50 ,,
Carbon monoxide	− 140° C.	39 ,,

It will be noticed that the five gases in the table have very low critical temperatures; these gases and hydrogen were until recently called *permanent* gases, because until 1879 all attempts to liquefy them had failed owing to the temperatures employed being above the critical point. Hydrogen and helium have the lowest critical temperatures of all gases and have only recently been liquefied by Dewar. The boiling point of hydrogen is as low as −238° C, liquid hydrogen is only $\frac{1}{14}$th the density of water.

Various methods have been employed in liquefying gases. Faraday was able to liquefy a large number of gases by means of their own pressure in glass tubes. To liquefy chlorine in this way the yellow crystals of chlorine hydrate, $Cl_2\ 8\,H_2O$, are brought into a glass tube of about 1 c.m. in diameter, and closed at one end. The tube is then bent at right angles at about its middle point and sealed. If now the sealed end be placed in a freezing mixture, whilst the other end containing the hydrate be gently warmed, a comparatively large volume of chlorine is liberated, and the pressure of the accumulated gas together with the low temperature employed is sufficient to bring about its liquefaction.

If silver chloride be saturated with ammonia gas, it forms the compound $2\,AgCl.\ 3\,NH_3$, and this body treated in the same way evolves ammonia in such a quantity as to liquefy by its own pressure.

Diffusion of gases.—The particles of gases possess a much greater freedom of motion than do those of liquids or solids, for the excursions which they may make are confined in the case of the latter to the space occupied by the liquid or solid itself; in the case of gases, however, the extent of these excursions is only limited by the walls of the vessel in which they are contained. Furthermore, if the walls are loose and open in texture, that is, porous, then it is possible for the gaseous particles to traverse them.

If a quantity of ammonia be discharged at one end of a room, the odour of the gas will, after a short time, be perceptible at the other end, even though the temperature of the room is constant throughout and the air still and free from currents.

That a very light gas should rise in a denser atmosphere and a heavy gas fall, is only what might be expected from the experience gained with solids or liquids. The following experiments will, however, serve to show that gases, however light they may be, will also gradually diffuse *downwards* through a denser atmosphere, and however heavy they may be, they will gradually diffuse *upwards* through a lighter atmosphere. The particles of a gas must therefore be subject to some other impetus than that accounted for by the ordinary laws of gravitation. The transfer of a mass of a gaseous body (hydrogen or coal gas in a balloon) takes place, it is true, in accordance with gravitation, but *diffusion* of the particles of gases cannot be so explained; it is the result of an active and incessant motion proper to the particles themselves.[1]

If a stout glass collecting jar of about $\frac{1}{4}$ litre content is filled with hydrogen and held steadily, mouth downwards, for three or four minutes and a lighted taper is then brought into it; it will be found that instead of burning quietly, as pure hydrogen does, there will be an explosion. This is evidence that during the period of exposure, the heavier air particles have diffused into the jar, the explosion being due to admixture of oxygen with the hydrogen. If three similar bottles are filled with chlorine and their mouths closed with stoppers and they are then placed in beakers as shown in the figure and the mouths of the beakers covered with glass plates; on removing the stoppers from two of them the following observations can be made.

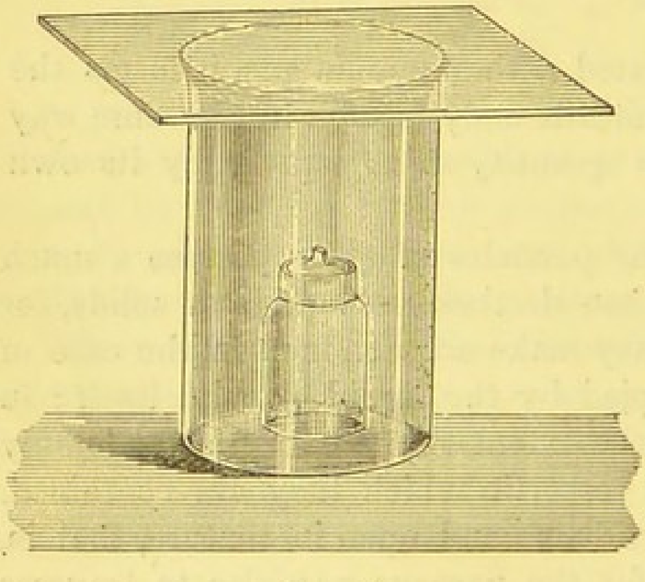

FIG. 2.

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[1] This statement must not, however, be taken to indicate that the constitution of gases differs essentially from that of liquids and solids. The *particles* of liquids and possibly solids also partake of progressive movements, but these are more limited in extent, being restricted to the mass of the liquid or solids; they also give evidence of being less rapid.

(1) In a few minutes aspirate some of the air from the beaker through a solution of potassium iodide ; the solution will be coloured brown owing to the fact that chlorine liberates iodine from a solution of potassium iodide. Air will not do this, and evidence is thus presented that some of the chlorine, though more than twice as heavy as air, has passed from the bottle into the surrounding space.

(2) Compare the colour of the second unstoppered bottle from time to time with that of the one remaining stoppered, the green colour in the former will be seen to grow much more faint owing to the gradual diffusion of the chlorine from the bottle into the beaker.

A porous cell, such as is used in voltaic batteries, is fitted with an indiarubber stopper, and a glass tube about half a metre long, furnished with a bulb, is passed through the stopper ; this is bent and drawn out into a jet as shown in the figure. Before inserting the cork fill the bulb and lower part of the tube with water. Now place a beaker filled with hydrogen over the porous cell, and the water will be immediately depressed and driven out of the jet in a fine stream. This is evidence that the light gas hydrogen passes through the walls into the porous cell quicker than the air is able to pass out of it. A greater volume of gas collects within the space of the cell and tube and forces the water out before it.

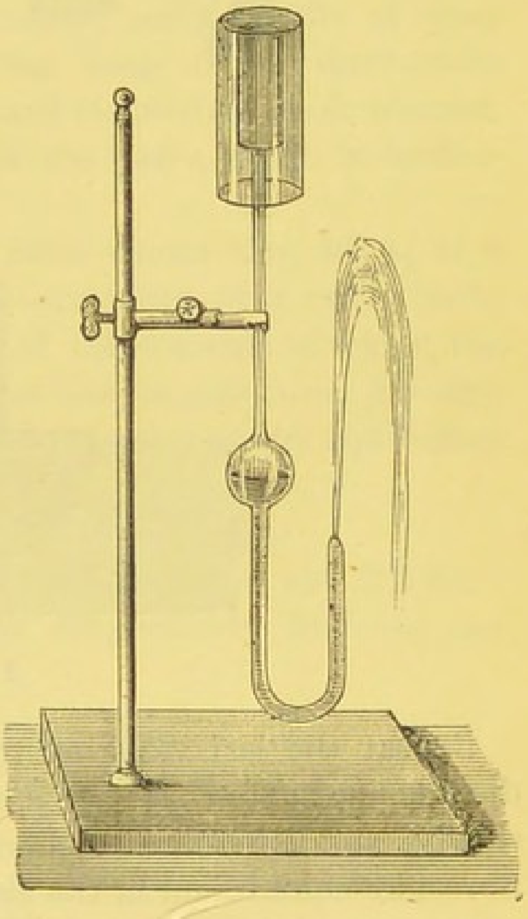


FIG. 2a.

Do a similar experiment with the arrangement shown in the figure 2b, in which it is possible to observe, by bubbles passing through the water in the bottle, that air is finding its way into the porous cell through the glass tube. In this case the cell containing air is surrounded with carbon dioxide in a beaker. Under such circumstances the air diffuses out of the cell quicker than the heavier gas, carbon dioxide, passes into it. This tends to produce a partial vacuum within the cell, and air enters in bubbles through the liquid in the bottle.

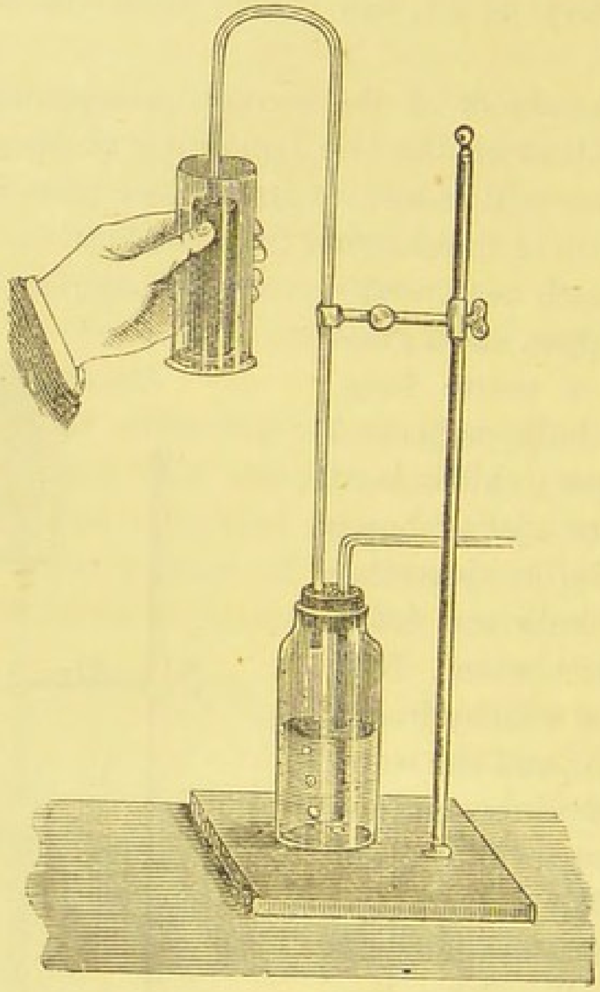


FIG. 2b.

Repeat the last experiment, using oxygen instead of carbon dioxide, and note that in this case the bubbles pass in much more slowly, and altogether a much smaller volume of air is required to restore equilibrium in the cell.

The relative densities of the gases employed in the above experiments are—

Hydrogen, 1.	Air, 14·4.	Carbon dioxide, 22.
		Oxygen, 16.

The greater the difference in density, the more rapid is the diffusion. By measuring the amount of different gases which diffused through a porous plug in a given time, under like conditions, Graham found that *the relative rate of diffusion is inversely proportional to the square root of their densities.* Thus in relation to air—

		$\frac{1}{\sqrt{\text{density}}}$.	Velocity of diffusion observed.
Density of hydrogen	= 0·0695	= 3·792	3·830
„ oxygen	= 1·1043	= 0·951	0·949
„ carbon dioxide	= 1·5180	= 0·812	0·812

The Metric System of Weights and Measures.

Before entering into further detail in regard to the relative density of gases, it will be well to adopt certain units of mass and volume. The metric system has been found convenient for all operations in which weighing and measuring are concerned.

The *unit of length* in this system is the *metre*, which is equivalent to 39·37 inches.

The *unit of volume* is that of a cube whose side is $\frac{1}{100}$ of a metre, equivalent to very nearly one-sixteenth of a cubic inch, and the *unit of weight* is the weight of this volume of water, the temperature being that at which water has its maximum density, viz. 4° C. This weight is termed the *gramme*, and is equivalent to 15·432 grains.

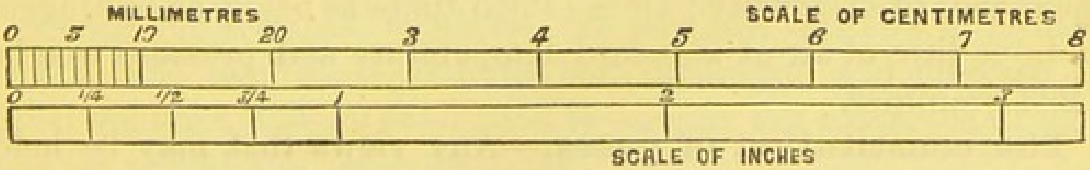
The prefix *kilo* indicates the multiple 1000, thus—

1 kilogramme = 1000 grammes = 15432 grains = abt. 2·2 lbs.

The prefixes *deci*, *centi*, and *milli* respectively indicate the fractional parts $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$.

1 decimetre = $\frac{1}{10}$ metre = 3·937 inches.
1 centimetre = $\frac{1}{100}$ „ = 0·3937 „
1 millimetre = $\frac{1}{1000}$ „ = 0·03937 „

One inch is thus slightly more than 25 millimetres.



1 decigramme = $\frac{1}{10}$ gramme = 1·5432 grains.
1 centigramme = $\frac{1}{100}$ „ = 0·15432 „
1 milligramme = $\frac{1}{1000}$ „ = 0·015432 „

A measure of volume very frequently employed is the *litre*, which is the volume occupied by a kilogramme of water; it is therefore equivalent to a cubic decimetre, or, in English measure, 61·027 cubic inches.

Whenever the specific gravity of a liquid or solid is spoken of, water is used as the standard of comparison; thus, if we say that sulphuric acid has a specific gravity of 1·84, we imply that it is 1·84 times as heavy as water, and hence one cubic centimetre of such acid will weigh 1·84 grammes.

Hydrogen is in like manner employed as the standard by which to express the density (or better, specific gravity) of gases. One litre of hydrogen at standard temperature and pressure (*i. e.* 0° C. and 760 m.m. mercury) weighs 0·0899 gramme, and when we say that nitrogen has a density of 14, we mean that it is 14 times as heavy as hydrogen; one litre of it should therefore weigh (0·0899 × 14) grammes.

In calculations bearing upon the weight and volume of gases, it is convenient to bear in mind the volume occupied (at 0° C. and 760 m.m.) by a gramme of hydrogen; this is, of course, $\frac{1}{0{\cdot}0899}$ litres, or 11·12 litres.

The volume occupied by 1 gramme of nitrogen is $\frac{1}{0{\cdot}0899 \times 14}$ litres, and by 14 grammes of nitrogen $\frac{14}{0{\cdot}0899 \times 14}$ litres, that is again 11·12 litres.

And in general, the volume occupied by x grammes of an elementary gas, when x is the atomic weight of the element, is 11·12 litres. It must be added that sometimes *air* is taken as the standard of density; air is 14·383 times as heavy as hydrogen, and one litre of air at standard temperature and pressure weighs 1·293 grammes.

The constitution of gases.—Any views that may be held relating to the constitution of gases must be consistent with the following observations—

(1) No difference in physical character is found to exist between gases that are elements and those that are compounds. In either case they expand or contract, as the temperature and pressure vary, in accordance with the laws of Charles and Boyle. There is, indeed, every reason to believe that the constitution of simple and compound gases is similar.

(2) That the smallest portion of matter attainable by any process of subdivision or capable of taking part in a chemical change is not infinitely small (Dalton's atomic theory).

(3) Gay Lussac showed that when gases combine together they do so in volumes which bear a simple ratio to one another and to that of the product. The relative volumes which do so combine are also found to be represented by small whole numbers.

Thus actual experiment shows that—

2 vols. of hydrogen and 1 vol. of oxygen combine to form 2 vols. of water vapour.
1 vol. of hydrogen and 1 vol. of chlorine combine to form 2 vols. of hydrochloric acid gas.
2 vols. of carbon monoxide and 1 vol. of oxygen combine to form 2 vols. of carbon dioxide.
1 vol. of nitrogen and 3 vols. of hydrogen combine to form 2 vols. of ammonia.

that is

1 vol. of water vapour is formed from	1 vol. of hydrogen and ½ ,, ,, oxygen.
1 ,, hydrochloric acid ,, ,,	½ ,, ,, hydrogen and ½ ,, ,, chlorine.
1 ,, carbon dioxide ,, ,,	1 ,, ,, carbon monoxide and ½ ,, ,, oxygen.
1 ,, ammonia ,, ,,	1½ ,, ,, hydrogen and ½ ,, ,, nitrogen.

Hence, for instance, whatever the smallest particle of hydrochloric acid may be, it contains both hydrogen and chlorine in equal volumes, and we shall have to assume the existence of still smaller particles of these elements.

Three striking and important features are thus evident—

(*a*) that the constitution of *all* gases is similar;

(*b*) that the ultimate particles of matter have actual and definite dimensions;

(*c*) that we must conceive of two kinds of particles.

Avogadro's hypothesis affords an explanation that is consistent with the behaviour of simple and compound gases, and at the same time in consonance with Dalton's theory of the indivisibility of the ultimate particle known as the atom.

Avogadro recognized two kinds of ultimate particles—

(*a*) the ultimate particle which can exist in the free state, as for instance the smallest particle of gaseous hydrochloric acid. This we term the *molecule.*

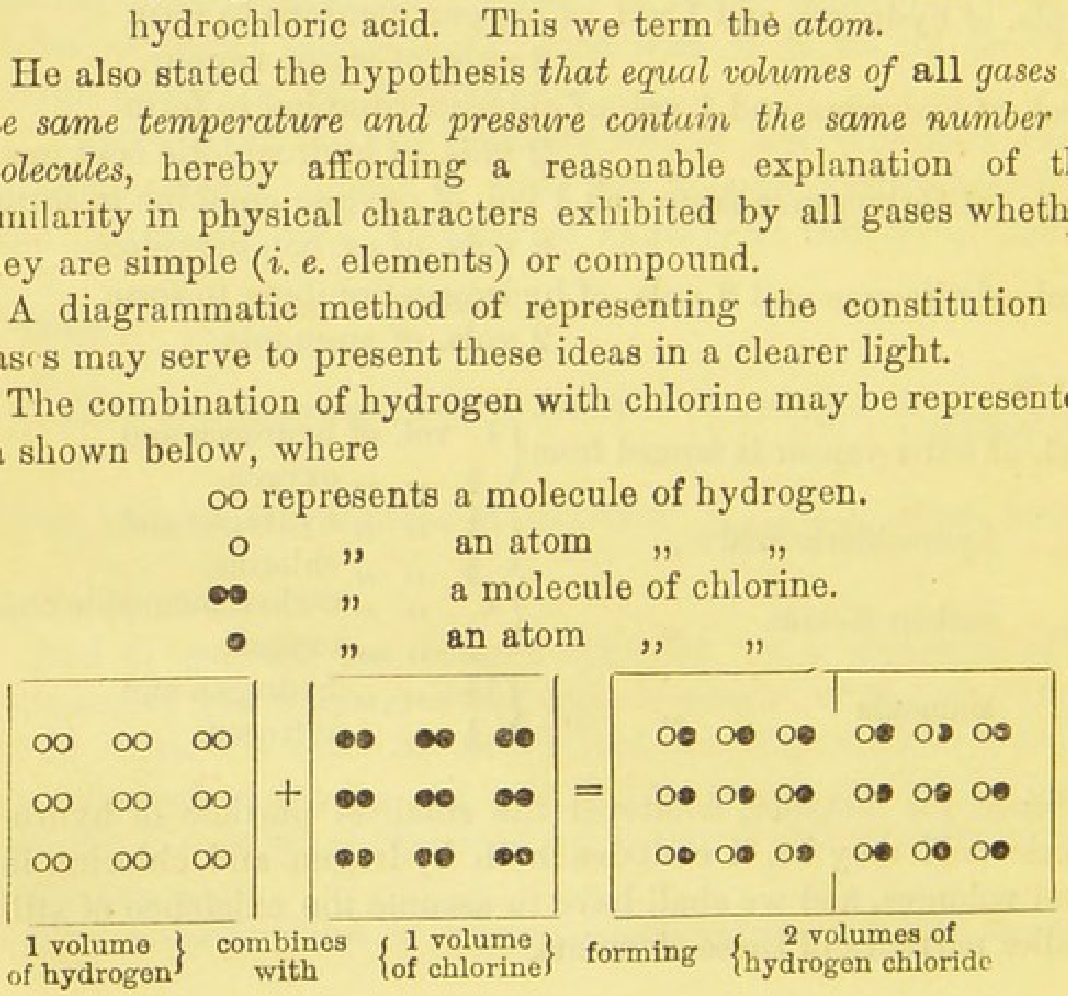
(*b*) the ultimate particle which is capable of taking part in a chemical change, or capable of being transferred from one chemical compound to another, as, for instance, the hydrogen or the chlorine contained in the molecule of hydrochloric acid. This we term the *atom.*

He also stated the hypothesis *that equal volumes of* all *gases at the same temperature and pressure contain the same number of molecules,* hereby affording a reasonable explanation of the similarity in physical characters exhibited by all gases whether they are simple (*i. e.* elements) or compound.

A diagrammatic method of representing the constitution of gases may serve to present these ideas in a clearer light.

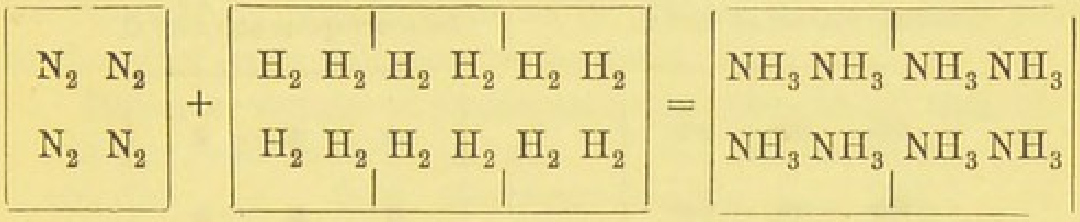
The combination of hydrogen with chlorine may be represented aa shown below, where

oo represents a molecule of hydrogen.
o „ an atom „ „
●● „ a molecule of chlorine.
● „ an atom „ „



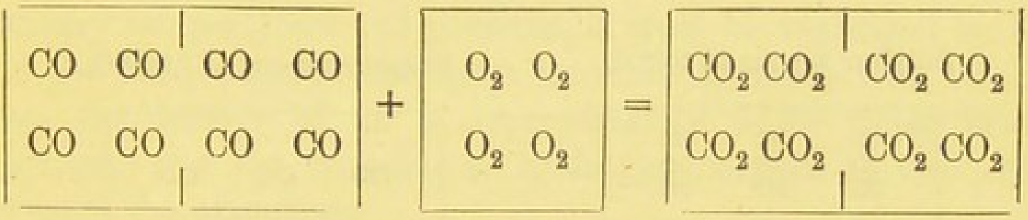
The volume represented is such as to be that occupied by nine molecules, but the explanation holds equally well whatever number of molecules might be taken.

Also representing the molecule of nitrogen by N_2
" " " hydrogen by H_2
" " " ammonia by NH_3
and taking for equal volumes the mean space occupied by 4 molecules

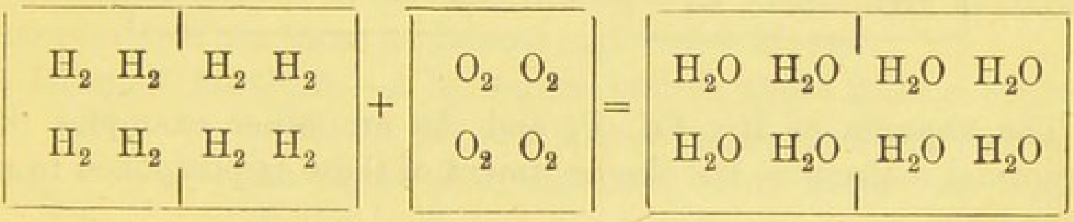


1 volume of nitrogen combines with 3 volumes of hydrogen forming 2 volumes of ammonia

Similarly



2 volumes of carbon monoxide combine with 1 volume of oxygen forming 2 volumes of carbon dioxide



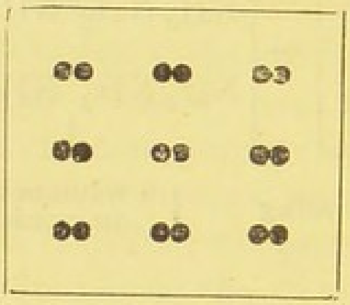
2 volumes of hydrogen combine with 1 volume of oxygen forming 2 volumes of water vapour

The conception of the constitution of simple and compound gases indicated in these diagrams will be found to accord with the observations of Gay Lussac, and the hypothesis of Dalton and Avogadro.

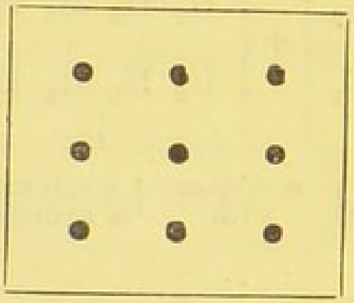
In the gases mentioned above it has been assumed that the molecule consists of two atoms, and though as a rule this assumption is borne out by the facts, there are certain exceptional cases in which it does not hold. Instances of this are afforded in the case of iodine vapour at very high temperatures, in which the molecule consists of *one atom ;* and sulphur vapour, just above the boiling point of sulphur (at 500° C.), in which the molecule consists of *six atoms.*

The representation of these cases may be made as follow—

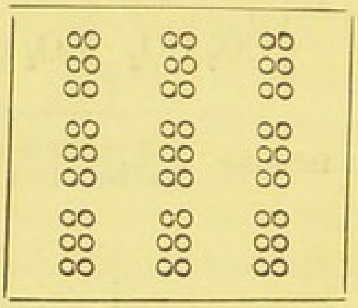
Iodine vapour at 450° C.



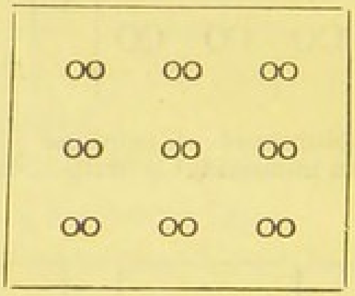
Iodine vapour at 1,500° C.



Sulphur vapour at 500° C.



Sulphur vapour at 1,000° C.



The vapours of Hg, Cd, P, and As are other examples of abnormal molecules, but the treatment of these is postponed to a later stage.

The molecular weight of gases.—In speaking of the density of gases, it is most usual to adopt that of hydrogen, the lightest of gases, as the standard of comparison, and to designate the density of hydrogen as unity. The density of gases can then be determined in the manner described at the beginning of this chapter. It will be found from actual experiment that

Hydrogen being taken as 1·0 the density of

nitrogen	is 14·0	oxygen	is 15·9
chlorine	,, 35·4	hydrogen chloride	,, 18·2
ammonia	,, 8·5	carbon dioxide	,, 22·0 and so on.

As equal volumes of the respective gases contain the same number of molecules, then the weight of the molecule must be *proportional* to that of the weight of equal volumes of the gases, *i.e.* proportional to the density.

The weight of the *atom* of hydrogen having been taken as 1, the *molecule* H_2 must be taken as 2. Hence the *molecular weight* of the other gases will likewise be doubled—

Molecular weight of hydrogen being taken as 2·0 that of

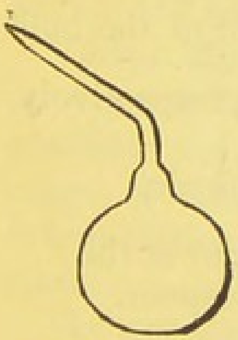
nitrogen	will be 28·0	oxygen	will be 31·8
chlorine	,, ,, 70·8	hydrogen chloride	,, ,, 36·4
ammonia	,, ,, 17·0	carbon dioxide	,, ,, 44·0 and so on.

Determination of Vapour Density.—Where the substance is a gas the vapour density may be determined by the method already described (p. 1), but where it is a solid or liquid at ordinary temperatures and pressure, it must be vaporized by heat, and the comparison is then most conveniently made with air ; and since the density of air is approximately 14·45 times that of hydrogen, and the molecule of hydrogen consists of two atoms, we have the expression

$$\text{Molecular weight} = 28{\cdot}9\,D$$

where D is the density of the gas *compared with air*. The chief methods employed in the determination of the density at higher temperatures are those of Dumas and Victor Meyer.

Dumas' Method.—A light glass bulb of about 200 c.c. content is drawn out to a fine point in the form shown in the figure and weighed. This gives the weight of the bulb (*w*) filled with air, temperature and pressure being noted. By gently warming the bulb, and then placing the orifice beneath the surface of the liquid whose vapour density is to be determined, and allowing the bulb to cool again, a quantity of the liquid is introduced. This should be in considerable excess of that required to fill the whole bulb with vapour, as it is necessary to ensure the air



being expelled from the bulb in the process of volatilization; usually 5 to 10 cubic centimetres will suffice. The bulb is now placed in a bath of heated liquid, the temperature of which is kept constant, and at least 20° above that of the boiling point of the liquid under examination. When it is seen that the whole of the liquid has been transformed into vapour, the orifice of the bulb is sealed at the blowpipe. We have now, presumably, the glass bulb quite filled with the vapour; after cooling and carefully cleaning, it is weighed. This gives the weight of the bulb ($w_{\prime}$) with the vapour required to fill it at the temperature of the bath.

A small portion of the sealed orifice is now broken off under water; the vapour having condensed, the water rushes in and should completely fill the bulb. It is then wiped dry and weighed again along with the piece broken off. This gives the weight of the bulb ($w_{\prime\prime}$) filled with water.

The weight of 1 c.c. of air is

$$\frac{0{\cdot}001293 \times 273 \times p}{(273 + t) \times 760}$$

where p is the pressure and t the temperature at the first weighing, and that of 1 c.c. of water being 1 gramme, the relation between these (approximately $\frac{1}{800}$) is known, and we shall represent it by R.

Then if the (unknown) weight of the vacuous bulb be represented by W, we have

$$w - \mathrm{W} = \mathrm{R}\,(w_{\prime\prime} - \mathrm{W})$$

$$\text{from which } \mathrm{W} = \frac{w - \mathrm{R}w_{\prime\prime}}{1 - \mathrm{R}}$$

We are now in a position to ascertain the *actual* weights of air and the vapour in the bulb by deducting the weight of the bulb $\frac{w - \mathrm{R}w_{\prime\prime}}{1 - \mathrm{R}}$ from the weighings of the bulb w and $w_{\prime}$ respectively, thus:—

$$w - \frac{w - \mathrm{R}w_{\prime\prime}}{1 - \mathrm{R}} = \frac{(w_{\prime\prime} - w)\,\mathrm{R}}{1 - \mathrm{R}} = \text{weight of the air,}$$

$$\text{and } w_{\prime} - \frac{w - \mathrm{R}w_{\prime\prime}}{1 - \mathrm{R}} = \frac{w_{\prime} - w + (w_{\prime\prime} - w_{\prime})\,\mathrm{R}}{1 - \mathrm{R}} = \text{weight of the vapour.}$$

When these values are corrected for temperature (the pressure may be taken as not varying during the experiment) the density of the vapour (D) as compared with air will be found to be—

$$\frac{w_{,} - w + (w_{,,} - w_{,})\,\mathrm{R}}{(w_{,,} - w)\,\mathrm{R}} \times \frac{273 + t_{,}}{273 + t}$$

where t is, as before, the temperature at the first weighing, and $t_{,}$ the temperature of the bath.

Several minor corrections have been omitted in the foregoing description, but they affect the result very slightly, and it must be remembered that a high degree of accuracy cannot be attained by this method, and is indeed unnecessary, since the main purpose in view is to decide whether the molecular weight of a given substance be M or some multiple or submultiple of M.

Dumas' method cannot be used at any temperature approaching the point at which glass begins to soften (say over 400°), and is thus only applicable to liquids of low boiling point.

By substituting porcelain or metal for glass, as has been done by Deville and Troost and others, and heating the bulb in the vapour of sulphur (444°) or stannous chloride (606°) or other substances, the method is more widely applicable; by means of a gas furnace a temperature of 1700° has been attained and the vapour density of some metals such as zinc, cadmium and of many salts such as aluminium chloride, ferric chloride, etc., has been determined. There is no essential difference in the nature of the observations to be made, though where a gas furnace is used, some means must be adopted for regulating and for measuring the temperature employed, and in addition to this it is desirable to replace the air in the bulb by nitrogen or some inert gas, since at high temperatures oxygen in most cases attacks the substance.

Victor Meyer's method.—This is the only other method of importance used in the examination of inorganic bodies, and it possesses the advantage of being applicable over a considerable range of temperature; it is also easy to manipulate and the determination can be made with a small quantity of the substance.

The apparatus is represented in the figure. It consists of a rather wide glass tube (*a*) narrowed in the upper part and then widened again near the top so as to admit an india-rubber stopper, the whole length of the tube being 600 m.m. Near the top of the narrow portion there is a side tube (*b c*) of the form shown. An outer jacket of copper (*d*) is provided of about the same length as the tube; in this is placed a quantity of water, naphthalene or other substance suitable for heating the glass bulb, according to the temperature required to volatilize the substance under examination, the bulb being so placed as to leave a clear space round it. A graduated tube (*e*) is filled with water and inverted over the end of the side tube. The cork being inserted in its place the jacket is heated and the temperature

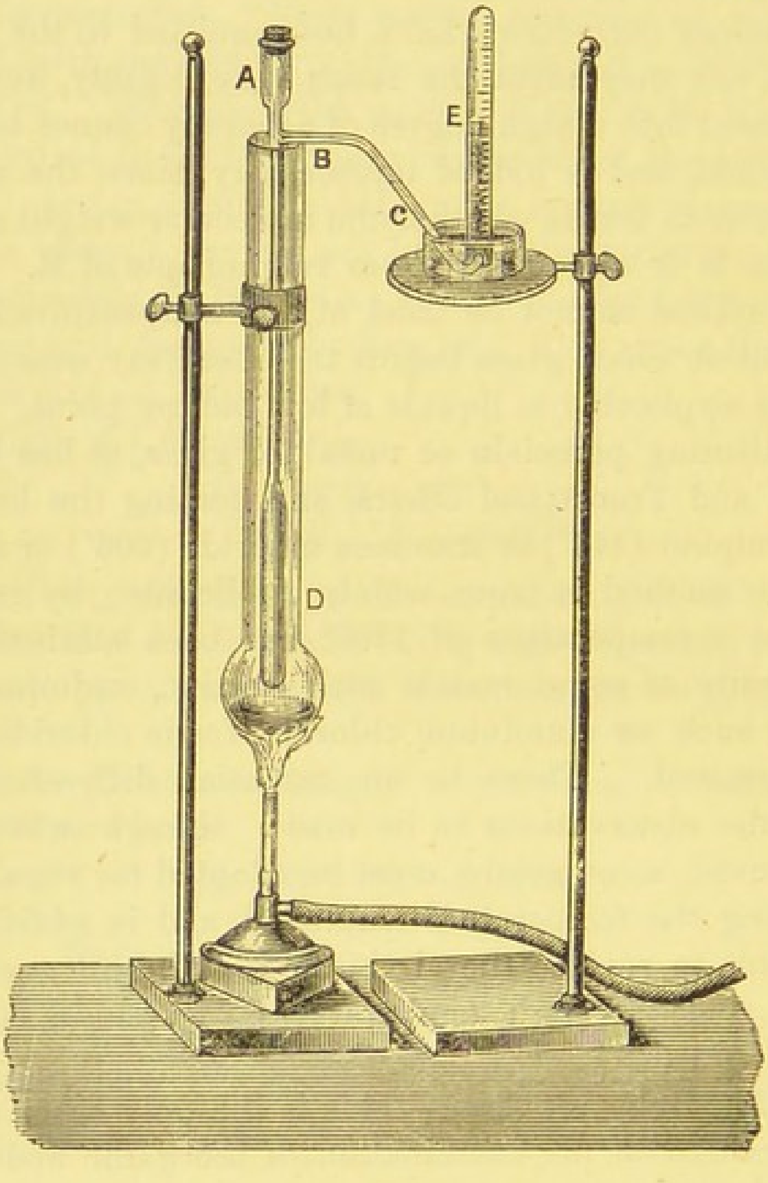


FIG. 3.

of the glass tube raised in this way to that of the vapour of the bath, 100° (water) or 217° (naphthalene), etc., as the case may be. Owing to the expansion of the air, bubbles pass out into the graduated tube.

When the temperature becomes constant the bubbles cease, and the cork is then withdrawn and a weighed amount (about 0·1 to 0·2 grm.) of the substance in a small bottle or bulb is dropped in[*] and the cork immediately replaced. If the experiment is successful, the substance will be very rapidly vaporized and an equivalent volume of air will be expelled by the side tube. This is carefully measured in cubic centimetres and the temperature (t) and pressure (p) of the room at the time is noted. Reduced to standard temperature and pressure this will give the volume which the vapour would occupy at standard temperature and pressure thus—

$$V = \frac{v \times 273 \times (p - s)}{(273 + t) \times 760}$$

s being the tension of aqueous vapour at the temperature t. This is the volume occupied by the weight (w) of the substance taken, when transformed into vapour, and it is easily seen that D the density compared with air will be—

$$D = \frac{w}{0·001293\ V};$$

as compared with hydrogen it will be—

$$D_1 = \frac{w}{0·0000896\ V}.$$

Provided only that the temperature of the jacket is constant and sufficiently high to ensure rapid vaporization of the substance, the actual temperature employed need not be known. This will be clear if we remember that the volume of the air which is actually displaced and collected at the graduated tube is at the temperature of the room; the vapour of the substance occupies precisely the volume which this air would have occupied at the temperature of volatilization. We have therefore the

---

[*] A little sand should be put in the bottom of the tube to prevent it being broken when the bulb is dropped in, also a device may be used by which the substance may be dropped into the tube without removing the cork.

volume which the vapour would occupy if it could be collected at the temperature of the room.

When it is required to determine the vapour density of bodies which require a very high temperature to vaporise them, a platinum vessel must be substituted for the glass tube and a gas furnace for the bunsen burner.

CONSTITUTION OF COMPOUNDS IN THE GASEOUS CONDITION.

The inquiry into the nature and constitution of the molecule of any gaseous compound may be carried out along several independent lines.

We may ascertain—

(1) the vapour density, and deduce from this the molecular weight;

(2) the products formed when the compound is dissociated or decomposed by heat or other agencies;

(3) the steps by which the compound may be synthesized or built up either from its elements or from simpler compounds;

(4) the behaviour of the compound in the presence of suitable reagents.

The effect of heat.—If a compound should exist at ordinary temperatures in the gaseous condition,—or if, though solid or liquid, it may be transformed into the gaseous condition,—it can easily be ascertained whether it behaves as a typical gas or not. For, then, as we have already seen, it expands regularly and equally with each equal increment of temperature. In other words, if two axes are drawn at right angles, and along one is plotted the volume occupied by the gas, and along the other its temperature at the time of measurement, the line passing through all the points so determined will be a straight line. The volume of the gas at 0° C. being v, its volume at the temperature t will be

$$\frac{v(273+t)}{273}$$

the pressure remaining constant.

Its density will be $D = \frac{W}{\omega}$

where W = the weight of a given volume of the gas, and ω is the weight of the same volume of hydrogen, measured under the same conditions of temperature and pressure. Or if, as is frequently the case, air be used instead of hydrogen as the medium of comparison, and the density be then found equal to d, then the density (D) compared with hydrogen is—

$$D = 14{\cdot}45\, d,$$

and the molecular weight of the compound will be—

$$2\,D \text{ or } 28{\cdot}9\, d$$

The methods by which the vapour density (and hence the molecular weight of a compound) is determined are the same as those already described in Chapter I. of this book.

Dissociation.—In many cases, however, as the temperature increases, a point is reached at which the volume occupied is greater than it should be according to Charles' law, and the density shows a corresponding diminution. For instance, stannous chloride, if it be of the composition Sn_2Cl_4, should have the vapour density 188·8, whilst as $SnCl_2$ its vapour density would be 94·4. It boils at 606° C., and at 619° its vapour density was found to be 185·5, corresponding very nearly to Sn_2Cl_4, but as higher temperatures were employed the vapour density diminished, till at 800° C. it was 104, approaching to the value for $SnCl_2$, but still being too high for this.

The vapour density of stannous chloride indicates that about the boiling point its molecule is Sn_2Cl_4, at higher temperatures these heavier molecules gradually dissociate into $SnCl_2$, but at 800° C. (and even at 1100° C.) the complete dissociation into the $SnCl_2$ molecules has not been effected.

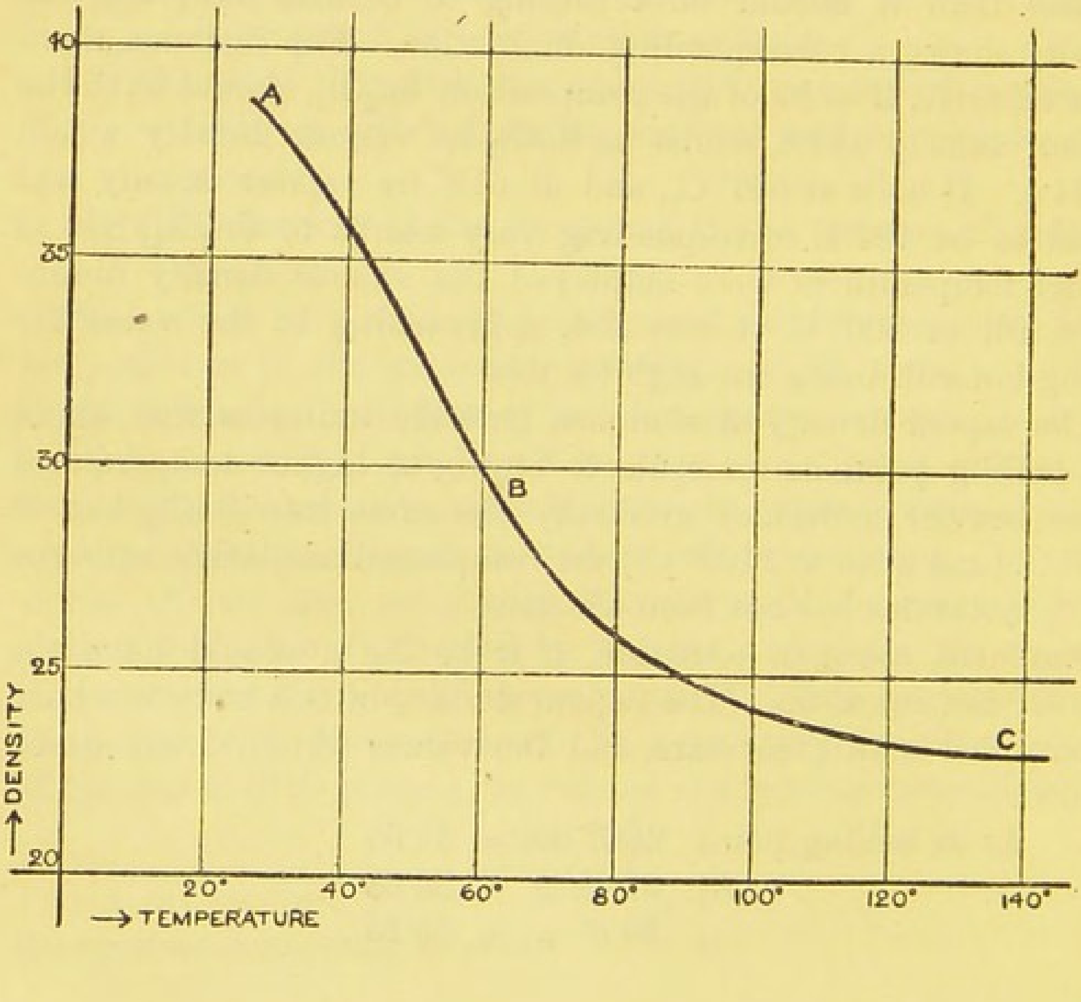
Similarly, nitrogen tetroxide, if it be N_2O_4, should have the vapour density 45·95. The vapour density of this body has been determined with great care, and the values obtained are given below :—

At its boiling point 26·7° D = 38·30
At 35·4° „ = 36·56
„ 39·8° „ = 35·25

At 49·6° „ = 32·80
„ 60·2° „ = 30·16
„ 70·0° „ = 27·84
„ 80·6° „ = 26·01
„ 90·0° „ = 24·85
„ 100·1° „ = 24·27
„ 111·3° „ = 23·70
„ 121·5° „ = 23·41
„ 135·0° „ = 23·12
About 140·0° „ = 22·98

Now 22·98 is the vapour density corresponding to the composition NO_2. It appears, therefore, that at about 140° C. nitrogen tetroxide is fully dissociated, thus—

$$\underset{\text{1 molecule.}}{N_2O_4} = \underset{\text{2 molecules.}}{2\,NO_2.}$$



Even at its boiling point, the density is much lower than the 45·95 required by the formula N_2O_4, so that when it passes into the state of vapour it is in a state of partial dissociation.

In the foregoing diagram, these numbers have been plotted on a curve A B C, and it will be evident that this breaking up of the N_2O_4 molecules into NO_2 molecules does not take place in direct proportion to the increase of temperature; at B the curve is steepest, showing that at about 70° C. the change takes place most rapidly, whilst at the lower temperatures the dissociation is less rapid, as shown at A; as the state of existence as NO_2 is approached, the fall is also much less marked. So far, we have regarded dissociation as the gradual breaking down a gas composed of complex molecules into simpler molecules; we have seen that the pressure being constant, the extent to which this occurs depends on the temperature. We may add that dissociation curves are, as a rule, similar in character to that given in the above figure, showing, at the earlier and later stages, a slower transition, and midway between these a maximum rate of transition.

Extent of dissociation.—From the observations (assuming that N_2O_4 and NO_2 are the only products), the number of molecules of each of these may be calculated. Let there be at the outset 100 molecules N_2O_4, and of these at a given temperature, say, 49·6° C., x are dissociated, forming $2\,x$ molecules of NO_2, and leaving $(100 - x)$ undissociated molecules of N_2O_4; 100 N_2O_4 become $(100 - x)\,N_2O_4 + 2\,x\,NO_2$.

There are now $(100 + x)$ molecules in place of the original 100, and the density will have diminished in the inverse proportion, so

$$\text{at } 49{\cdot}6^\circ\text{ C. } \frac{100}{100 + x} = \frac{32{\cdot}8}{45{\cdot}95}$$

from which we calculate $x = 40$.

At 49·6° C., therefore, the gas consists of—

60 molecules of N_2O_4
80 ,, NO_2.

The pressure which a gas exerts on the walls of a confined space is directly proportional to the volume of the gas (as measured under standard conditions) which is introduced into that space by means of pressure; hence instead of determining the volume occupied by the gas at different temperatures, the increase of pressure may be measured, and the volume estimated from this. This method of procedure is very frequently adopted, especially where high temperatures have to be employed.

Dissociation accompanied by chemical change.—In the cases already discussed, the changes which occur as the temperature rises are reversed as the temperature falls again, the NO_2 molecules again gradually reunite to form N_2O_4 molecules, so that starting at 140° C. with 200 molecules of NO_2, there will be again 60 molecules of N_2O_4, and 80 molecules of NO_2 when the temperature has fallen to 49·6° C. The process may be represented—

$$N_2O_4 = NO_2 + NO_2 \text{ for rising temperature,}$$
$$NO_2 + NO_2 = N_2O_4 \text{ for falling temperature.}$$

Such reversible changes may conveniently be written as a general equation—

$$N_2O_4 \rightleftarrows NO_2 + NO_2.$$

Many compound substances, when heated, undergo a change of composition thus—

$$\begin{aligned} 2\,Ag_2O &= 4\,Ag + O_2 \\ PCl_5 &= PCl_3 + Cl_2 \\ CaCO_3 &= CaO + CO_2. \end{aligned}$$

The conditions may be such that re-combination takes place as the temperature is lowered; this, though not always possible, is known to occur in the last two cases—

$$\begin{aligned} PCl_3 + Cl_2 &= PCl_5 \\ CaO + CO_2 &= CaCO_3 \end{aligned}$$

Dissociation of phosphorus pentachloride.—The phenomena observed with nitrogen tetroxide, in regard to molecules of a like chemical composition, take place here between molecules of an unlike composition, and are likewise classed as dissociation phenomena. Thus if phosphorus pentachloride be heated in a closed tube the vapour acquires a greenish tinge although the vapour of phosphorus pentachloride itself is colourless. This is due to the presence of free chlorine. On cooling, re-combination takes place gradually and the greenish tinge disappears.

A most interesting observation was made by Wurtz, who found that if PCl_5 be heated in an atmosphere of either of the products of dissociation, viz., PCl_3 or Cl_2, then it was possible to vaporize the PCl_5 without decomposition occurring. The effect of heating phosphorus pentachloride *alone* is therefore expressed by—

$$\overset{\text{1 molecule}}{PCl_5} = \overset{\text{1 molecule}}{PCl_3} + \overset{\text{1 molecule}}{Cl_2}.$$

Hence the vapour density was indeed found to be 52·6, instead of 104 as required by the formula PCl_5.

Heated in presence of PCl_3 or Cl_2, the vapour density was 104, corresponding to the formula PCl_5.

Dissociation of calcium carbonate.—In this instance we have a typical case of the dissociation of a solid substance ($CaCO_3$) into the solid oxide of calcium (CaO) and the gaseous carbon dioxide (CO_2). The dissociation tension of CaO is so small that it may be neglected, and the extent of the dissociation may be measured by the pressure exerted when calcium carbonate is heated in a closed space. Le Chatelier has determined this pressure at various temperatures and found it—

at 547° C. = 27 m.m. of mercury.
„ 610° C. = 46 „ „
„ 625° C. = 56 „ „
„ 740° C. = 255 „ „
„ 745° C. = 289 „ „
„ 810° C. = 678 „ „
„ 812° C. = 763 „ „
„ 865° C. = 1333 „ „

The pressure exerted by the gas at each temperature is termed the *dissociation tension* for that temperature; thus at 812° C. the dissociation tension is 763 m.m. of mercury, approximately standard atmospheric pressure. On cooling, re-combination of the CaO and CO_2 occurs just as in the previous cases. So if the temperature be allowed to fall from 810° C. to 610° C. this re-combination takes place until the dissociation tension 46 m.m., corresponding to 610° C., is reached, and if the temperature be kept at this point, the dissociation tension will remain at 46 m.m. If then calcium carbonate be heated *under* *such conditions that the products formed remain in contact*, the phenomena observed are true dissociation phenomena. In the ordinary process of lime burning, the carbon dioxide is continually passing off and ultimately only CaO is left; here we have *chemical decomposition.*

Dissociation of Ammonium Chloride.—That ammonium chloride when heated breaks up into ammonia and hydrochloric acid may easily be shown by dropping a fragment of ammonium chloride into a red hot platinum crucible. A moistened (red) litmus paper held just over the mouth of the crucible will be turned blue owing to the fact that the ammonia being lighter rises quicker than the hydrochloric acid gas and at a little height predominates in quantity so as to act on the litmus paper. Or again if a jar of ammonia and one of hydrochloric acid gas be brought together mouth to mouth, the two gases rapidly combine forming a fine white powder consisting of ammonium chloride. So when ammonium chloride is heated it breaks up into ammonia and hydrochloric acid and at ordinary temperatures these gases recombine to form ammonium chloride. The dissociation may be more distinctly shown by heating a little ammonium chloride in a glass tube closed with corks through which passes the stem of a clay pipe. When a gentle current of air is passed through the clay pipe and directed on to a moistened litmus paper it will be turned blue, since the lighter gas (ammonia) diffuses more rapidly through the walls of the porous pipe.

Other cases of dissociation.—The vapour density of sulphuric acid is only one half of what it should be as calculated from the formula H_2SO_4. This difference is due to the fact that it is dissociated into molecules of H_2O and SO_3. If some of the acid is heated in a vessel with a capillary orifice, the water vapour being less dense than the SO_3 vapour diffuses more quickly and the acid is after a time found to contain an excess of SO_3.

Sulphur vapour which just above the boiling point consists of molecules having the composition S_6 above 1000 C. is composed of molecules having the composition S_2.

Iodine vapour below 700° consists of molecules containing two atoms above 1500°, the molecules are monatomic.

DETERMINATION OF THE COMPOSITION OF GASES.

Composition of sulphur dioxide.—This may be determined by synthesis. By means of the arrangement shown (Fig. 4), a fragment of sulphur may be burnt in oxygen. The sulphur is fused on to thin platinum wire, and ignited by passing an electric current along the wire by which the wire is heated. The apparatus and the oxygen used in the experiment must be free from moisture. The gas in the globe at first expands owing to the heat of combustion, and forces the mercury up the further limb, but on cooling it returns to its original volume. It is seen therefore that during the combination of sulphur and oxygen to form sulphur dioxide no alteration in volume occurs, that is to say *sulphur dioxide contains its own volume of oxygen.* It follows then from Avogadro's hypothesis that one molecule of sulphur dioxide must contain one molecule of oxygen. Further, since the molecular weight of the gas as found by experiment is 64 the composition, according to the method given under sulphuretted hydrogen (see page 33), must be represented by the formula SO_2.

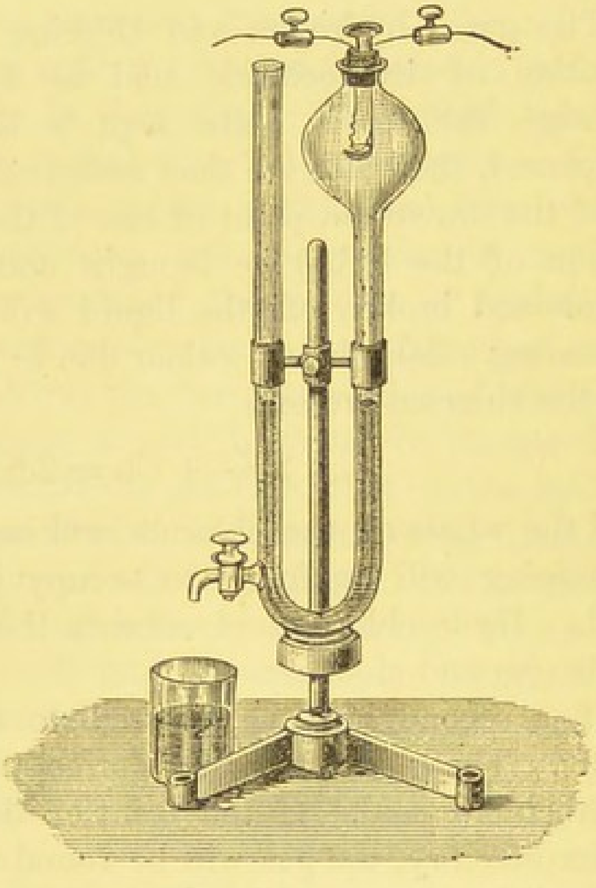


Fig. 4.

The composition of hydrochloric acid.—Hydrochloric acid may be decomposed by the electric current, but owing to the fact that chlorine dissolves in the liquid to a considerable extent, no satisfactory proof of the composition of hydrochloric acid can be arrived at in this way. If, however, the decomposition be allowed to go on until the liquid is saturated with chlorine, the gases hydrogen and chlorine are given off in the proportions in which they exist in hydrochloric acid. An elegant proof of the composition of hydrochloric acid is furnished by the following course of procedure.

The gases hydrogen and chlorine resulting from the decomposition of hydrochloric acid as described above are passed through thin glass bulbs kept in the dark until all the air is displaced, the bulbs are then sealed off.

If the drawn-out point of one of the bulbs (protected from the action of the light) be brought under a solution of potassium iodide and broken off, the liquid will gradually rise in the bulb, assuming a dark brown colour due to the liberation of the iodine by the chlorine present,

$$2\,KI + Cl_2 = 2\,KCl + I_2,$$

and the whole of the chlorine will be taken up. The hydrogen remaining will be found to occupy just half the volume of the bulb. Hydrochloric acid consists therefore of equal volumes of hydrogen and chlorine.

If a second bulb be exposed to diffused daylight for some hours. The hydrogen and chlorine will slowly combine to form hydrochloric acid. If the point of the bulb be now broken off under mercury, the gas will be found to occupy the same volume as it did before combination took place, but when dipped into water the hydrochloric acid gas will be absorbed readily, and the water will fill the bulb.

From these experiments we learn that one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid gas.

Composition of ammonia.—The composition of ammonia may be determined by passing the gas through a red-hot tube containing copper oxide. The hydrogen is transformed into water, which may be collected and weighed in the manner described on page 71, and the volume of nitrogen which passes forward may also be ascertained.

$$3\,CuO + 2\,NH_3 = 3\,Cu + 3\,H_2O + N_2.$$

The *volume* of hydrogen may be readily calculated from the weight of water obtained.

A second method depends on the fact that when electric sparks are passed through gaseous ammonia it is slowly decomposed into its constituents. Dry ammonia is passed into a eudiometer over mercury, and its volume accurately measured.

The sparks are then passed until no further increase in volume occurs; it will be found to be just *double* its original volume. If now excess of oxygen be passed into the eudiometer and the spark passed, the hydrogen will combine with it and form water, which condenses, leaving nitrogen and the *excess* of oxygen added, two-thirds the diminution being the volume of hydrogen.

This method is not very accurate owing to the fact that some of the nitrogen combines with oxygen, forming oxides of nitrogen. By the electrolysis of ammonia it may however be shown that the volume of nitrogen it contains is one-third that of the hydrogen. The experiment is performed in the following manner. A saturated solution of common salt is prepared, and to this is added about one-tenth of its volume of strong ammonia. The solution is now introduced into a voltameter fitted with carbon electrodes and submitted to the action of the current from six Bunsen cells. Nitrogen collects in one tube and hydrogen in the other, and the volumes will be found to be in the proportion 1 : 3.

Composition of nitric oxide.—When iron is heated in nitric oxide in combines with the oxygen and sets free the nitrogen. The gas first expands by the heat, and the iron when it burns takes up the oxygen from the nitric oxide. On the completion of the reaction only nitrogen remains, and this gas will be found to occupy half the volume of the original gas. Hence one molecule of nitric oxide contains one atom of nitrogen, and its formula will be N_1O_x. To determine the value of x we must ascertain the density of nitric oxide compared with hydrogen. It will be found to be fifteen times as heavy as hydrogen, and since the hydrogen molecule, H_2, weighs 2, the molecule of nitric oxide must weigh 30, that is, the molecule consists of NO.

The composition of carbon monoxide may be ascertained by exploding the gas in a eudiometer along with oxygen. It will be found that 100 volumes of CO and 100 volumes of oxygen after explosion show a contraction to 150 volumes, and on absorbing the carbon dioxide formed, by means of potash, 50 volumes of oxygen will remain. Thus 100 volumes of carbon monoxide have united with 50 volumes of oxygen to form 100 volumes of carbon dioxide, according to the equation—

$$\underbrace{2\,CO}_{\text{4 vols.}} + O_2 = \underbrace{2\,CO_2}_{\text{4 vols.}}$$

Carbon monoxide is fourteen times as heavy as hydrogen, and therefore the molecule of hydrogen being 2, that of carbon monoxide is 28. Its composition is therefore represented by the formula CO.

The composition of carbon dioxide may be shown by a method similar to that employed in the case of sulphur dioxide. Thus when carbon is burnt in oxygen no change of volume occurs, and carbon dioxide is therefore said to contain its own volume of oxygen. Moreover, if a known weight of diamond, a very pure form of carbon, be burnt in oxygen, and the carbon dioxide formed be weighed, the relation between the weight of carbon taken and that of carbon dioxide obtained will be found to be 12 : 44, or 12 parts by weight of carbon unite with 32 parts by weight of oxygen. On this evidence the formula for carbon dioxide must be CO_2, or some multiple of this. But as the molecular weight of carbon dioxide is 44, the composition is that represented by the formula CO_2.

Composition of Sulphuretted Hydrogen.—Sulphuretted hydrogen when heated either alone or in contact with metallic tin yields its own volume of hydrogen, that is, the hydrogen set free occupies (under the same conditions of temperature and pressure) the same volume as the sulphuretted hydrogen from which it has been obtained.

Now according to the hypothesis of Avogadro, equal volumes of gases under like conditions of temperature and pressure contain the same number of molecules. Hence *one molecule of sulphuretted hydrogen yields and contains one molecule of hydrogen.*

As yet we have not determined the number of atoms of sulphur in the gas. Call this number for the present x, and so—

$$H_2S_x \text{ on decomposition} = H_2 + S_x.$$

We have a ready means of ascertaining the relation of the sulphur to the sulphuretted hydrogen by comparing its density with that of hydrogen and determining the molecular weight of the gas; this we find to be 34, and so—

Molecular weight of sulphuretted hydrogen	...	34
" " " hydrogen contained in it	...	2
Weight of sulphur in the molecule by difference	...	32

But 32 is the atomic weight of sulphur, hence the molecule of sulphuretted hydrogen contains one atom of sulphur—the value of x is 1, and the equation given above becomes—

$$H_2S \text{ on decomposition} = H_2 + S,$$

and the composition of the gas is represented by the formula H_2S.

The decomposition of sulphuretted hydrogen by metallic tin is represented by the equation—

$$2\,H_2S + Sn = 2\,H_2 + SnS_2,$$

Composition of nitrous oxide.—The composition of the gas may be determined by the combustion of potassium in it, and by an estimation of its density, the proof corresponding with that already given in previous cases. The potassium may be heated in the gas as shown in Fig. 5. It will be found to contain its own volume of nitrogen—

$$\underset{\text{4 volumes.}}{2\,N_2O} = \underset{\text{4 volumes.}}{2\,N_2} + O_2.$$

Or it may be mixed with excess of hydrogen, and exploded in a eudiometer, when the reaction is—

$$N_2O + H_2 = H_2O + N_2.$$

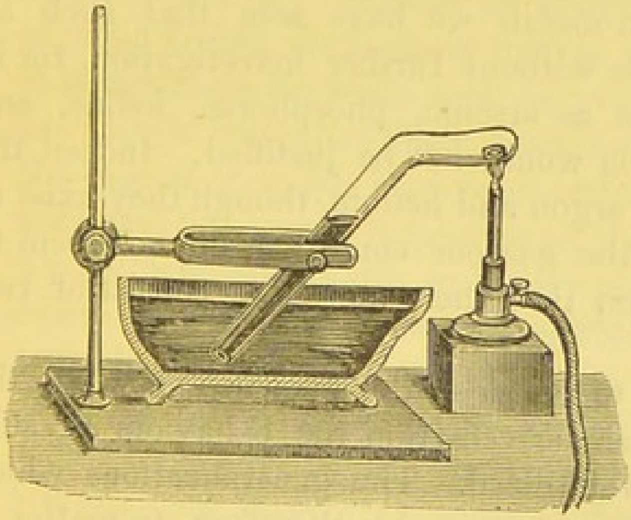


Fig. 5.

CHAPTER II.

THE ATOMIC WEIGHTS OF THE ELEMENTS.

The atomic weight as determined by direct observations of the vapour density of the element.—It has already been mentioned that some of the elements which exist at ordinary temperatures in the solid or liquid condition, may be vaporized and the density of the vapour determined by the methods previously described. If we assume that the molecule of the vapour consists of two atoms, then the atomic weight may be arrived at immediately from the vapour density. In the previous pages when treating of the non-metals we have seen that such an assumption cannot be made without further investigation, for in the case of such elements as arsenic, phosphorus, iodine, and sulphur, such an assumption would not be justified. Indeed the recently-discovered bodies, argon and helium, though they exist at ordinary temperatures in the gaseous condition, do not seem to fall in with the assumption that their molecules consist of two atoms.

We shall now be able to consider the evidence on which the atomic weights are based, as derived from the behaviour of substances which cannot be volatilized. The generalizations which are to be drawn under this section apply, therefore, to matter in the solid or liquid condition. One most important physical property, the determination of which assists in ascertaining the true atomic weight, is specific heat.

Specific heat.—If equal masses (say 50 grms.) of different metals are heated to the same temperature, say 100° C., and if each is then placed separately in 100 cc. of water at 0°, the water will not be raised to the same temperature in each case, for some metals require more heat than others to bring them to a given temperature and consequently give out more on cooling again.

The same remark applies to other bodies besides metals. The heat evolved by unit weight of a large number of gases, liquids, and solids on cooling through the same number of degrees has been determined, and it has been found that water gives out the most heat; it is therefore taken as standard, and other bodies compared with it. *The specific heat* of a body is the ratio of its thermal capacity to that of water taken as unit. It may be determined by placing a known weight of the substance, usually at 100° C., in a known weight of water at 0°C., and observing the rise in temperature produced in the latter when the substance and liquid have the same temperature. In the case of gases, the gas at a constant pressure and at a known temperature is passed through a spiral surrounded by cold water and the rise in temperature of the water is noted.

Specific heat of the elements as related to atomic weight.—In the year 1819, Dulong and Petit published an account of a large number of determinations of the specific heat of solid bodies, particularly metals, and drew attention to the fact that these specific heats were in general inversely proportional to the atomic weight. There were notable exceptions, however, in the case of zinc, tin, lead, iron, and some other elements. "Still," they say, "the mere inspection of the numbers obtained, points to a relation so remarkable in its simplicity as to be at once recognized as a physical law, susceptible of being generalized and extended to all elementary substances. In fact, the products in question, which express the capacities for heat of atoms of different nature, are so nearly the same for all, that we cannot but attribute these very slight differences to unavoidable errors, either in the determination of capacities for heat or in the chemical analyses." They thus deduced from their observations the generalization that "the atoms of all simple bodies have precisely the same capacity for heat."

The adoption of this generalization by chemists led to the alteration of a number of the then-accepted values for atomic weight. This of course was followed by changes in the formulæ of the compounds derived from these elements. In all instances, however, where revision has taken place, the effect has been to bring out in a clearer light the relations which the elements and their compounds show to one another, and to throw them into natural groups, in which striking resemblances are shown between the members of the same group. It is on this ground that the generalization of Dulong and Petit has appealed so strongly to chemists. In the following table we give the atomic weights and specific heats of a number of the commoner elements, and also the product of the atomic weight multiplied by the specific heat (the so-called "atomic heat"), this being in most cases practically a constant, whose value is approximately 6·4.

	Atomic weight. A.	Specific heat. C.	A.C.
Sodium ...	23·0	0·293	6·7
Magnesium ...	24·0	0·250	6·0
Aluminium ...	27·0	0·214	5·8
Phosphorus ...	31·0	0·174	5·4
Sulphur ...	32·0	0·178	5·7
Potassium ...	39·0	0·166	6·5
Calcium ...	39·9	0·170	6·8
Chromium ...	52·4	0·121	6·3
Manganese ...	54·8	0·122	6·7
Iron	55·9	0·114	6·4
Copper... ...	63·2	0·095	6·0
Zinc	65·1	0·094	6·1
Arsenic ...	74·9	0·081	6·1
Bromine ...	79·8	0·084	6·7
Silver	107·7	0·057	6·1
Tin	118·8	0·055	6·5
Antimony ...	119·6	0·051	6·1
Iodine	126·5	0·054	6·8
Platinum ...	194·3	0·032	6·3
Gold	196·7	0·032	6·4
Mercury ...	199·8	0·032	6·4

	Atomic weight.	Specific heat.	
	A.	C.	A.C.
Lead	206·4	0·031	6·4
Bismuth ...	207·3	0·030	6·4
Uranium ...	239·0	0·028	6·7

The above may all be regarded as consistent with Dulong and Petit's generalization, which may be stated thus:—*That the atomic weight of an element, multiplied by its specific heat, is a value approximating very nearly to* 6·4.

There are, however, notable exceptions, which we have not yet accounted for; these are—

Carbon ... A.C. = 1·8
Hydrogen ... ,, = 2·3
Boron ... ,, = 2·7
Beryllium ... ,, = 3·7
Silicon ... ,, = 3·8
Oxygen ... ,, = 4·0

Observations made by Weber in 1875, on the behaviour of carbon, boron, and silicon, have shown that the specific heat of these elements increases as the temperature rises, and at a certain limit it remains almost constant through a considerable range of temperature, thus:—

from 800° C. to 980° C. A.C. for carbon = 5·5
at 600° C. ,, boron = 5·5
from 130° C. to 230° C. ,, silicon = 5·7

Also Humpidge found similarly the value of A.C. for beryllium to be 5·6 at 400° C. to 500° C.

Finally, it must be remembered that the generalization of Dulong and Petit is not to be used as a means of ascertaining or of applying corrections to the atomic weight as determined from the results of the analysis of definite compounds, for the degree of accuracy attainable is very much greater in the latter case. What it does enable one to do is to decide between certain alternative values, all of which satisfy the relations deduced from analysis.

As an example of the application of Dulong and Petit's generalization, let us refer to the example on page 39, where an examination of the composition and vapour density of a chloride of tin has led to the acceptance of the formulae Sn_4Cl_4, Sn_2Cl_4 and $SnCl_4$, if the atomic weight of tin is taken as 29·3, 58·5 and 117·1 respectively. Dulong and Petit's generalization renders it possible to decide between these numbers.

The specific heat of tin has been found to be 0·056 and the product

A.C. is 1·64, if 29·3 be accepted as the atomic weight
,, ,, 3·28, ,, 58·5 ,, ,,
,, ,, 6·56, ,, 117·1 ,, ,,

It is evident, therefore, that 117·1 is the value to be adopted, and that $SnCl_4$ is the proper formula for the chloride of tin. These conclusions having been drawn, the formulae of the remaining salts of tin are easily deduced.

Specific heat of compounds.—Some years after Dulong and Petit had announced their results, Neumann called attention to the fact that the product of the specific heat × the atomic weight of compounds was practically the same for compounds of a like character; thus—

for $PbCl_2$ C. = 0·0664 A.C. = 18·4
,, $PbBr_2$ C. = 0.0533 A.C. = 19·6
,, PbI_2 C. = 0.0427 A.C. = 19·6
So for Aragonite $CaCO_3$ C. = 0·206 A.C. = 20·6
Strontianite $SrCO_3$ C. = 0·145 A.C. = 21·3
Witherite $BaCO_3$ C. = 0·109 A.C. = 21·4
Cerussite $PbCO_3$ C. = 0·080 A.C. = 21·3

The further conclusion drawn from these facts was that the specific heat remained materially the same whether the element were in the free state or in combination. The product A.C. for lead being determined directly, and found to be 6·4, that for the haloid elements could be calculated thus—

$$\text{for chlorine it would be } \frac{18{\cdot}4 - 6{\cdot}4}{2} = 6{\cdot}0$$

$$\text{for bromine} \quad ,, \quad \frac{19{\cdot}6 - 6{\cdot}4}{2} = 6{\cdot}6$$

$$\text{for iodine} \quad ,, \quad \frac{19{\cdot}6 - 6{\cdot}4}{2} = 6{\cdot}6$$

In the same way it may be gathered that the "atomic heat" of $CaCO_3$, $SrCO_3$, $BaCO_3$, and $PbCO_3$ being almost identical, that of Ca, Sr, Ba, and Pb are also almost identical. By using this method, it is possible to ascertain the "atomic heat" of elements like oxygen, hydrogen and nitrogen, which would present extreme difficulty in the way of direct determination in the solid, or even liquid, condition.

The determination of the formula of a compound.— The compound is first subjected to the process of quantitative analysis by which the relative proportions of the constituent elements are ascertained. Thus stannic chloride was found to consist of tin and chlorine in the proportions:

Tin	45·4	per cent.	
Chlorine	54·6	„	„.

Taking it as established that the atomic weight of chlorine is 35·2, let us examine how the atomic weight of tin and the formula of stannic chloride may be arrived at. *Assuming that there are an equal number of atoms of chlorine and tin present in the compound* we can determine the atomic weight of tin thus:

$$\text{Chlorine}\ \frac{54{\cdot}6}{35{\cdot}2} = 1{\cdot}551,$$

and x being the atomic weight of tin

$$\frac{45{\cdot}4}{x} = 1{\cdot}551,$$

$$x = 29{\cdot}27.$$

And this would be the case if the accepted formula were SnCl or Sn_2Cl_2, or Sn_3Cl_3, or in general Sn_nCl_n.

Similarly, *assuming that there are two atoms of chlorine for each atom of tin* we shall have for the atomic weight of tin (x'):

$$\frac{45.4}{x'} = 0.775$$

$$x' = 51.54$$

The formulae possible under this assumption would be $SnCl_2$, Sn_2Cl_4 or in general Sn_nCl_{2n}.

So, *assuming three atoms of chlorine for each atom of tin* we should have for the atomic weight of tin, (x''):

$$\frac{45.4}{x''} = 0.517$$

$$x'' = 87.81$$

which would hold for $SnCl_3$, Sn_2Cl_6 or in general Sn_nCl_{3n}.

Or finally *assuming four atoms of chlorine for each atom of tin* we have for the atomic weight of tin, (x''') :

$$\frac{45.4}{x'''} = 0.388$$

$$x''' = 117.08$$

which would hold for $SnCl_4$, Sn_2Cl_8 or in general Sn_nCl_{4n}.

All that we are able to decide from a quantitative analysis of the compound is that if the

atomic weight is 29.27 the formula is Sn_nCl_n
„ „ 58.54 „ Sn_nCl_{2n}
„ „ 87.81 „ Sn_nCl_{3n}
„ „ 117.08 „ Sn_nCl_{4n}

Further data are required and the next step is to find the vapour density of the compound. This proves to be 129 and the molecular weight is therefore 258.

We can now fix the value of n in the above table and thus reduce the alternative formulae to Sn_4Cl_4, Sn_2Cl_4, $Sn_{1\frac{1}{3}}\,Cl_4$, $SnCl_4$. The third of these is excluded as inconsistent with the atomic theory, and we have to decide between

Sn_4Cl_4, atomic weight of tin = 29.27
Sn_2Cl_4, „ „ = 58.54
$SnCl_4$, „ „ = 117.08

We now fall back as previously remarked on the generalization of Dulong and Petit that the product of the atomic weight and the specific heat should be approximately 6.4.

Electrolysis as a means of determining the "equivalent" weight of the elements.—If a strip of zinc and one of platinum be placed in dilute sulphuric acid, and connected together outside the liquid by metallic wires (say platinum), a current of electricity will be transmitted along the wires. No change of composition is effected thereby in the wires themselves. If we connect the ends of the wires by means of a strip of any metal, the current will pass through it also without effecting any permanent change.

If, however, a drop of sodium sulphate solution be placed on litmus paper, and the ends of the wires be brought into this, but not into contact with each other, it will be found that near the wire which is connected with the zinc, the paper will become blue from the presence of alkali, and near that connected with the platinum it will become red from the presence of acid. Of bodies which conduct a current of electricity we therefore recognize two classes—

(1) those which conduct electricity, but themselves undergo no change of composition; they are termed "*conductors.*"

(2) those which conduct electricity and undergo decomposition; they are termed "*electrolytes.*"

To the former class belong most of the elements; the latter consists of compounds either in the fused condition or in solution.

The solution of sodium sulphate in the foregoing experiment is an electrolyte and is decomposed during the passage of the electric current, the products formed in presence of water being caustic soda, which turns the litmus paper blue, and sulphuric acid, which turns it red.

Such a process of decomposition is called "electrolysis," and the parts of the wires which are in contact with the electrolyte are termed electrodes, being distinguished as the positive electrode or "*anode*" attached to the platinum, and the negative electrode or "*kathode*" attached to the zinc.

The phenomena which take place during electrolysis are usually of a complex character. For instance, there is ground for the assumption that sodium sulphate breaks up primarily into sodium and SO_4; these however cannot exist in presence of water, on which they react as follows :—

$$Na_2 + 2\,H_2O = 2\,NaOH + H_2$$
$$SO_4 + H_2O = H_2SO_4 + O$$

The caustic soda and the sulphuric acid remain in the liquid, whilst at the kathode *hydrogen* is set free, and at the anode *oxygen.* If sulphate of copper solution be electrolyzed, the copper does not react upon the water but deposits on the kathode, oxygen as before being liberated at the anode.

Faraday found that if a current be passed through a solution, the *amount* of the element liberated or deposited at the electrode in a given time was directly proportional to the strength of the current. If the same current were passed through solutions of different salts, then the amounts of the elements set free at the electrode always showed a definite relation to one another.

For instance, if the same current be passed through (*a*) acidulated water, (*b*) a solution of silver nitrate, (*c*) a solution of cupric sulphate, and the amount of hydrogen liberated by (*a*) = 0·01038 grm., then the amount of silver deposited from (*b*) was 1·118 grms. and of copper from (*c*) was 0·3281 grm.

If now we divide the values for (*b*) and (*c*) by that for hydrogen we obtain—

$$\frac{1 \cdot 118}{0 \cdot 01038} = 107 \cdot 7 \text{ for silver.}$$

$$\frac{0 \cdot 3281}{0 \cdot 01038} = 31 \cdot 6 \text{ for Copper.}$$

Such numbers may be termed the "Electrochemical Equivalents." A more complete list is given in the following table alongside the atomic weights.

	Equivalent.	Atomic Weight.
Potassium	39·0	39·0
Sodium	23·0	23·0
Gold	65·4	196·2
Silver	107·7	107·7
Copper	31·6	63·2
Mercury	99·9 and 199·8	199·8
Tin	29·5 and 59·0	118·0
Iron	28·0 and 56·0	56·0
Zinc	32·5	65·0
Lead	103·2	206·4
Oxygen	8·0	16·0
Chlorine	35·4	35·4
Bromine	79·8	79·8
Iodine	126·5	126·5
Nitrogen	4·7	14·0

An examination of the table shows—

(1) That the atomic weight is either equal to the electrochemical equivalent or some multiple of it.

(2) That, in some cases, the same element gives more than one value.

With regard to the first point, it must be remembered that the value obtained is the *equivalent as related to hydrogen.* And, as will be more fully explained on the next page, if we look upon the salts as resulting from salts of hydrogen (the acids), by replacement of the hydrogen by metals, then in case of some metals the atom replaces one atom of hydrogen, whilst in others it may replace two, three, or four atoms of hydrogen.

Metals are thus classified according to their power of replacing hydrogen as monovalent, divalent, trivalent and tetravalent.

The *equivalent* of a metal, as determined from its replacement of hydrogen, is therefore equal to

$$\frac{\text{Atomic Weight}}{\text{Valency}} = \text{for silver } \frac{107{\cdot}7}{1} = 107{\cdot}7$$

$$\text{for copper } \frac{63{\cdot}2}{2} = 31{\cdot}6$$

$$\text{for gold } \frac{196{\cdot}2}{3} = 65{\cdot}4 \text{ and so on.}$$

These numbers are the same as those determined for the electrochemical equivalents.

As to the second point, viz., that an element may have more than one equivalent, there is again a parallel in the replacement of hydrogen. The three metals given as examples, mercury, tin and iron, each form two independent series of salts; to take simply the chlorides of these elements, we have—

Mercurous chloride	$HgCl$	Stannous chloride	$SnCl_2$	Ferrous chloride	$FeCl_2$
Mercuric ,,	$HgCl_2$	Stannic ,,	$SnCl_4$	Ferric ,,	$FeCl_3$

1 atom of mercury in	mercurous	salts replaces	1 atom	of hydrogen	in HCl
,, ,,	mercuric	,,	2 atoms	,,	,,
1 atom of tin in	stannous	salts replaces	2 ,,	,,	,,
,, ,,	stannic	,, ,,	4 ,,	,,	,,
1 atom of iron in	ferrous	,, ,,	2 ,,	,,	,,
,, ,,	ferric	,, ,,	3 ,,	,,	,,

There are thus two equivalents for these metals.

$$\text{For mercury } \frac{199{\cdot}8}{1} \text{ and } \frac{199{\cdot}8}{2}$$

$$\text{For tin } \frac{118}{2} \text{ and } \frac{118}{4}$$

$$\text{For iron } \frac{56}{2} \text{ and } \frac{56}{3}$$

And, as in the previous case, the values so obtained agree with the electrochemical equivalent.

The atomic weight of an element is thus equal to the electrochemical equivalent, as determined during the electrolysis of a compound, multiplied by the valency of the element in the compound.

The replacement of hydrogen by other elements. If we regard the acids as salts of hydrogen, and other salts as formed by replacing hydrogen, the most cursory inspection of the formulae of a series of salts will show that the elements differ in respect of the number of atoms of hydrogen which they replace. For instance, we have the formula Na_2SO_4 and $CaSO_4$; in the former each atom of hydrogen in H_2SO_4 is replaced by *one* atom of sodium, in the latter one atom of calcium replaces *two* atoms of hydrogen. Extending the examination we see that—

(1) One atom of Na or K replaces *one atom* of H.
(2) „ „ „ Cu, Mg, Ca, &c., replaces *two atoms* of H.
(3) „ „ „ Al replaces *three atoms* of H.

A similar examination of other series of salts, such as the phosphates or carbonates, will lead to like conclusions. Moreover it may be shown by actual experiment that 23[1] grms. of Na or 39 grms. of K will liberate from water *one gramme* of hydrogen; 63·2 grms. of Cu or 24 grms. of Mg, etc., will liberate *two grammes* of hydrogen; 27 grammes of Al will liberate *three grammes* of hydrogen. If we inquire what weight of these metals will liberate *equivalent* weights of hydrogen, the values obtained with sodium and potassium will be proportional to the atomic weight, with Cu, Mg, etc., proportional to *half the atomic weight,* with Al proportional to *one-third the atomic weight.* Numbers in such relations to the atomic weight are termed *equivalent weights*, and the equivalent weights of Na and K are 23 and 39 respectively, in other words atomic weight is identical with the equivalent weight; these elements are therefore termed *monovalent.*

The *equivalent weights* of Cu, Mg, etc., are 31·6, 12, &c., and the atomic weight is double the equivalent weight; these elements are therefore termed *divalent.* The equivalent weight of Al is 9, and the atomic weight is threefold the equivalent weight; Al is therefore termed *trivalent.*

Regarding the acids as salts of hydrogen, we may derive the formulæ of the metallic salts by replacing hydrogen according to the equivalency of the metal in question; thus—

Nitric acid,	HNO_3	Nitrates,	KNO_3, $Cu(NO_3)_2$, $Al_2(NO_3)_6$.
Carbonic acid,	H_2CO_3	Carbonates,	K_2CO_3, $KHCO_3$, $CuCO_3$, $MgCO_3$.
Phosphoric acid,	H_3PO_4	Phosphates,	K_3PO_4, K_2HPO_4, KH_2PO_4, $Ca_3(PO_4)_2$, $AlPO_4$.

NUMERICAL RELATIONS BETWEEN THE ATOMIC WEIGHTS.

Prout's hypothesis.—In the early part of the century, Prout found from an examination of the atomic weights of the elements as then known, that in a large number of cases they were represented by *whole numbers* or values approaching very near to whole numbers.

The idea that all matter consists merely of different aggregates of one and the same original substance had possessed philosophers for many centuries, and it came to be formulated in more definite terms by Prout, the primary substance being regarded as hydrogen. The degree of accuracy to be attached to determinations of atomic weight was not such as to allow the hypothesis to be fully tested.

Stas undertook the re-determination of a number of atomic weights, using every possible precaution to ensure accuracy, in order to see whether they were really represented by whole numbers. A patient and thorough investigation convinced him that the hypothesis of Prout was untenable.

Döbereiner's triads.—A comparison of the atomic weights of certain groups of elements by Döbereiner, Dumas and others, led however to the recognition of the existence of certain relations between the values assigned to elements of the same chemical family.

Döbereiner's *triads* were groups of three elements of similar chemical character *showing the same or nearly the same differences of atomic weight—e. g.—*

	Atomic weight.	Common difference.
Lithium	7	
Sodium	23	16
Potassium	39	
Calcium	39·9	
Strontium	87·3	47·4
Barium	136·9	49·6
Sulphur	32	
Selenium	78·9	46·9
Tellurium	125	46·1
Chlorine	35·4	
Bromine	79·8	44·4
Iodine	126·5	46·7

Other relations of a like kind were pointed out by Dumas and others. It was noticed for instance that, taking a group of elements belonging to the same chemical family, the atomic weight of the middle member was the mean of the other two. Also that in such families the successive differences are approximately multiples of a common factor—*e. g.*—

Magnesium.	Calcium.	Strontium.	Barium.
24	40	87·5	137
= a	= a + 16	= a + 4 (16)	= a + 7 (16)
Oxygen.	Sulphur.	Selenium.	Tellurium.
16	32	79	125
= a	= a + 16	= a + 4 (16)	= a + 7 (16)

Such considerations led to a comparison being established between the elements and the homologous series of hydrocarbons—

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
16	30	44	58	72
= a	= a + 14	= a + 2 (14)	= a + 3 (14)	= a + 4 (14)

and so on.

A generalization of a more comprehensive kind was however made almost simultaneously by Lothar Meyer and by Mendelejeff, which applied, not to particular groups of elements, but to the whole of the known elements, and they arranged them in what is called the *periodic system*. This system brought out not only the numerical relations of the atomic weights but made it evident that the *properties* of the elements showed a similar periodicity. That is, not that any general relation could be established between the atomic value and these properties, but that the elements fell into *periods*, in each of which periods there was shown such a relation. Newlands had previously expressed this in an incomplete form, but it was reserved to Mendelejeff and Lothar Meyer to give to it its full development.

The following table gives the arrangement of Mendelejeff in periods, with a statement of the atomic weight—

Series.	Groups.							
	I	II	III	IV	V	VI	VII	VIII
1	H 1	—	—	—	—	—	—	
2	Li 7	Be 9·1	B 10·9	C 12	N 14	O 16	F 19	
3	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35·4	
4	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52·5	Mn 54·8	Fe Co Ni 56 58·6 58·6
5	Cu 63·2	Zn 65·1	Ga 69·9	Ge 72·3	As 75	Se 78·9	Br 79·8	
6	Rb 85·2	Sr 87·3	Y 89	Zr 90·4	Nb 94	Mo 96	—	Ru Rh Pd 103·5 104·1 105·5
7	Ag 107·7	Cd 111·7	In 113·6	Sn 118·8	Sb 120	Te 125	I 126·5	
8	Cs 132·7	Ba 136·9	La 138	Ce 140	—	—	—	
9	—	—	—	—	—	—	—	
10	—	—	Yb 172·6	—	Ta 182	W 183·6	—	Os Ir Pt 191 192·5 194·3
11	Au 196·7	Hg 199·8	Tl 203·7	Pb 206·4	Bi 207·3	—	—	
12	—	—	—	Th 232	—	U 239	—	

In this table, the elements are written in the order of their atomic weights, blanks being left where there is no corresponding element known. Since it was first formulated in 1869, the elements scandium (Sc), Gallium (Ga), and Germanium (Ge) have been discovered and are inserted in their proper places.

Numerical Relations.—It will be noticed that the atomic weights of elements occupying successive lines differ from one another by numbers which do not vary to any very great extent. In Series 3 for instance the successive values exceed those of Series 2 by approximately 16 units, whilst the members of Series 5 exceed those of Series 4 without much variation by about 25 units. Further examination will reveal many such regularities in this respect; the relations which had attracted the notice of Döbereiner and Dumas thus find a fuller expression in the table than these chemists had already given.

Chemical Character.—Running the eye along the horizontal rows or series one after another, it will be seen that the differences of chemical character are strikingly shown, the elements whose oxides are distinctly and strongly basic occurring on the extreme left, whilst those like the haloid elements and manganese, forming acidic oxides, occupy the extreme right. Excluding the consideration of Group VIII. for the present there is also, as we pass along the series, a gradual transition from the one character to the other.

If we now examine the several groups, taking each vertical column separately, it will be found that whilst there is a general resemblance prevailing throughout the group, it is the *alternate members* which exhibit the closest analogy. Thus Li, K, Rb, Cs; Be, Ca, Sr, Ba; Mg, Zn, Cd, Hg; P, As, Sb, Bi; S, Se, Te; Cl, Br, I, are all families of allied elements whilst there is a much less striking analogy between elements in juxtaposition, such as Cu and Rb, Ag and Cs, S and Cr, Cl and Mn, etc. It has come to be recognized that as expressive of close relationship, the alternative series must be grouped together. For the purposes of comparative study of the elements and their compounds it has, therefore, been found convenient to differentiate the series into the *odd series*, those indicated in the table by an odd number, and the *even series* indicated by an even number. The series may then be written in separate columns, thus for—

Group 1.		Group 2.		Group 3.		Group 4.	
Odd.	*Even.*	*Odd.*	*Even.*	*Odd.*	*Even.*	*Odd.*	*Even.*
H	Li	—	Be	—	B	—	C
Na	K	Mg	Ca	Al	Sc	Si	Ti
Cu	Rb	Zn	Sr	Ga	Y	Ge	Zr
Ag	Cs	Cd	Ba	In	La	Sn	Ce
—	—	—	—	—	Yb	—	—
Au	—	Hg	—	Tl	—	Pb	Th

Group 5.		Group 6.		Group 7.		Group 8.
Odd.	*Even.*	*Odd.*	*Even.*	*Odd.*	*Even.*	
					—	
—	N	—	O	—	F	
P	V	S	Cr	Cl	Mn	Fe. Co. Ni.
As	Nb	Se	Mo	Br	—	Ru. Rh. Pd.
Sb	—	Te	—	I	—	
—	Ta	—	W	—	—	Os. Ir. Pt.
Bi	—	—	U	—	—	

Valency.—The significance of this term has already been stated in general terms (see page 44). The valency of an element may usually be ascertained from a determination of the composition of its hydride or methide[1]; where no such compound exists, then the most stable oxide or chloride may be made use of for the purpose.

Thus, regarding hydrochloric acid, ClH, as the hydride of chlorine, we see that in it *one atom* of chlorine combines with *one atom* of hydrogen. So if we take the compounds sulphuretted hydrogen, SH_2, the hydride of sulphur and chloride of sulphur, SCl_2, we find *two atoms* of hydrogen and *two atoms* of chlorine respectively combining with one atom of sulphur. Or again, in the hydride and chloride of arsenic, AsH_3 and $AsCl_3$, we have *three atoms* of hydrogen and *three atoms* of chlorine combining with one atom of arsenic. Finally in the hydride of carbon (marsh gas) and chloride of carbon, CH_4 and CCl_4, we have *four atoms* of hydrogen and *four atoms* of chlorine combining with one atom of carbon. Nor can the atom of chlorine, sulphur, arsenic and carbon be made to combine with more than 1, 2, 3 and 4 atoms of hydrogen respectively to form stable and definite compounds. They are fully satisfied or *saturated*, and the compounds above spoken of are termed *saturated compounds.*

Now it has been experimentally shown that a measure of the chemical attraction or affinity exerted between two elements is afforded by the heat developed during their union. We must however carefully avoid the confusion of chemical affinity with valency. Valency is a property quite independent of affinity and peculiar to the individual elements. That arsenic requires three atoms of chlorine to form a saturated compound whilst sulphur is satisfied with two and hydrogen with one, by no means indicates that the affinity of arsenic for chlorine is greater than that of sulphur or hydrogen. Indeed in the majority of cases the opposite might be stated, namely, that the elements of greater activity which exhibit chemical affinity in the highest degree have the lowest valency, whilst inert bodies such as the elements in Groups IV. and VIII. often have the highest valency.

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[1] The methide is a compound of the element with one or more groups of the radical CH_3, and may in general be derived from the hydride by substituting CH_3 for H.

But now let us proceed to inquire how the valency of an element is arrived at. We have seen that hydrogen and chlorine are equivalent to one another, in regard to the number of atoms requisite to saturate other elements. Whatever their valency may be it is the same for both. A number of other elements agree with hydrogen and chlorine in this respect, but we know of no element which possesses a lower valency; that is, in no instance is it found that two or more atoms of any element combine with one atom of hydrogen to form a definite and stable compound. Hydrogen, chlorine and such elements as behave in the same way, may therefore be used as a kind of unit measure of valency, and are termed *monovalent* or *monad elements.* An element like sulphur which requires two atoms of hydrogen to saturate it, or which replaces two atoms of hydrogen, is *divalent* or a *dyad element,* and similarly arsenic and carbon are *trivalent* and *tetravalent* respectively, or *triad* and *tetrad elements.* We now see why the hydride (or the nearly related methide) and chloride are by preference used as means of determining valency. Oxygen, as indicated by the formula for water, H_2O, is divalent, and where the oxide is used as a means of estimating valency this must be borne in mind. Marsh gas, CH_4, for instance, points to carbon as being tetravalent, and just as much does CO_2 (each atom of oxygen being equivalent to two of hydrogen) indicate the tetravalency of carbon.

In the table given on p. 52, the valency of each of the elements is shown by the formula of a stable hydride or methide, or failing these a chloride or oxide.

Reviewing the compounds mentioned, we cannot fail to be struck with the periodic relation which occurs between valency and atomic weight. *In general* the members of—

Group	I	are	Monovalent.
,,	II	,,	Divalent.
,,	III	,,	Trivalent.
,,	IV	,,	Tetravalent.
,,	V	,,	Pentavalent or Trivalent.
,,	VI	,,	Hexavalent or Divalent.
,,	VII	,,	Heptavalent or Monovalent.
,,	VIII	,,	Octovalent to Divalent.

Series.	Groups.									
	I	II	III	IV	V	VI	VII	VIII		
2	$LiCl$	$BeCl_2$	BCl_3	CH_4	NH_3 N_2O_5	OH_2	FH			
3	$NaCl$	$MgCl_2$	Al_2Cl_6	$SiCl_4$	PH_3 P_2O_5	SH_2 SO_3	ClH $HClO_4$			
4	KCl	$CaCl_2$	Sc_2O_3	$TiCl_4$	$VOCl_3$	$CrCl_2$ CrO_3	$MnCl_2$ $KMnO_4$	Fe_2Cl_6	$CoCl_2$	$NiCl_2$
5	Cu_2Cl_2 $CuCl_2$	$ZnCl_2$	Ga_2Cl_6	$GeCl_4$	AsH_3 As_2O_5	SeH_2 $SeCl_4$	BrH			
6	$RbCl_2$	$SrCl_2$	Y_2O_3	$ZrCl_4$	$NbCl_5$	MoO_3	—	$RuCl_4$ RuO_4	Rh_2Cl_6 RhO_3	$PdCl_4$ PdO_2
7	$AgCl$	$CdCl_2$	In_2Cl_6	$SnCl_4$	$SbMe_3$ Sb_2O_5	TeH_2 TeO_3	IH HIO_4			
8	$CsCl$	$BaCl_2$	La_2O_3	CeF_4 CeO_2	—	—	—			
9	—	—	—	—	—	—	—			
10	—	—	—	—	$TaCl_5$	WCl_6	—	$OsCl_4$ OsO_4	$IrCl_4$ IrO_3	$PtCl_4$
11	$AuCl$ $AuCl_3$	$HgCl$ $HgCl_2$	$TlCl$ $TlCl_3$	$PbCl_2$ $PbMe_4$	$BiMe_3$	—	—			
12	—	—	—	$ThCl_4$	—	UCl_4 UO_3	—			

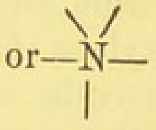
In the above table Me is adopted as an abbreviation for CH_3.

There are, however, compounds which prove exceptions to this general statement, and no complete expression of valency can be given without looking further into the constitution of chemical compounds. If our desire be merely to render an account of this subject for gaseous compounds or compounds which can be obtained without decomposition in the gaseous condition, and whose constitution is therefore more fully understood, then the task of assigning valency values is a simple one.

A full appreciation of the subject cannot, however, be gained without making a further inquiry as to *how the atoms are mutually arranged, and in what relation they stand to one another in the compound.* In order to do this, a symbolic method of representing formulæ has been widely adopted amongst chemists, which serves to give expression not only to the proportions in which the elements combine, but also to the distribution of the atoms within the molecule and mode of their attachment to one another.

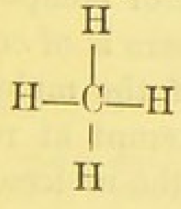
Graphic formulæ of volatile compounds.—The constitution and structure of the molecule, so far as it is known, may be represented in the following manner. The valency is indicated by means of lines in proximity to the symbol.

The molecule of hydrogen is H—H, the atom H—
„ „ oxygen is O=O, „ O= or —O—
„ „ nitrogen is N≡N, „ N≡ or

or N≣N, „ =N≡ or


These lines are merely symbols expressive of valency and may be drawn in any convenient position. Instances of their use in representing compounds are :—

Marsh gas.



$$\begin{array}{c}H\\ |\\ H—C—H\\ |\\ H\end{array}$$

Water.

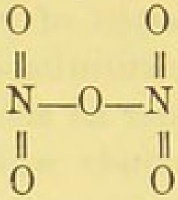
H—O—H

Carbon dioxide.

O=C=O

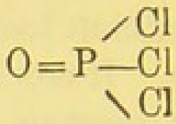
Ammonia.

Nitrogen pentoxide.

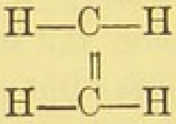


$$\begin{array}{ccccc} O & & & & O \\ \Vert & & & & \Vert \\ N & - & O & - & N \\ \Vert & & & & \Vert \\ O & & & & O \end{array}$$

Phosphorus oxychloride.

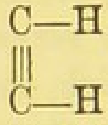


Unsaturated compounds.—There are certain compounds in which the valency is not exercised to the full extent; these are termed *unsaturated* compounds. For instance, though in the large majority of carbon compounds (as in marsh gas) carbon is tetravalent and associated with four atoms of hydrogen, in ethylene each atom of carbon is associated with two atoms of hydrogen only and in acetylene with one. Thus—



$$\begin{array}{c} H-C-H \\ \Vert \\ H-C-H \end{array}$$

Ethylene.



$$\begin{array}{l} C-H \\ \vert\vert\vert \\ C-H \end{array}$$

Acetylene.

It is assumed in such cases that certain valencies are suppressed or *latent*, the combining power remaining with the carbon atoms.

A very limited number of compounds occur in which this takes place even though they contain only one atom of the element showing latent valency, *e. g.*—

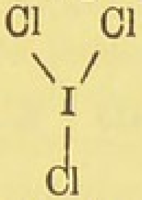
$=C=O$ Carbon monoxide.

$-N=O$ Nitric oxide.

Such bodies are usually characterized by the ease with which they enter into further combination with elements or groups of elements to form saturated compounds. Ethylene in presence of chlorine readily forms ethylene dichloride ($C_2H_4Cl_2$), and acetylene forms copper acetylide ($C_2H_2Cu_2O$), whilst carbon monoxide unites directly with chlorine to form phosgene gas ($COCl_2$), and with nickel to form nickel carbonyl $Ni(CO)_4$, and nitric oxide enters readily into association with ferrous salts and with chlorine, in the latter case forming nitrosyl chloride, NOCl.

Valency in solid compounds.—In the case of compounds which cannot be obtained in the state of vapour, there is of course much less known as to the actual constitution of the molecule, and very great uncertainty attaches to any attempt at representing the arrangement of the atoms composing the molecule.

And it is here in particular that the most embarrassing problems arise relating to valency. If iodine and chlorine are both monovalent how, for instance, are we to regard such a body as trichloride of iodine, ICl_3, or periodic acid, HIO_4, or perchloric acid, $HClO_4$? To take ICl_3 first; it is possible to look upon it as a compound of the same nature as ICl, in which case however iodine must be trivalent and the graphic formula—



or it may be regarded as a *molecular compound* of a molecule of ICl and a molecule of chlorine, Cl_2. Under such an assumption, we could write it—

I—Cl.Cl—Cl.

So, to take a more complex case of wide application, it may be asked what relation water of crystallization bears to the salt to which it is attached—*e.g.* in copper sulphate $CuSO_4.5H_2O$, or the alums, such as $K_2SO_4.Al_2 3SO_4.24H_2O$? Further than this, how can the very numerous and important class of bodies the silicates be represented? Although it is possible to express even such complex forms in a manner that will not do violence to the views of valency, as deduced from compounds of known constitution, it cannot be said that such representations throw additional light upon the structure of the molecule.

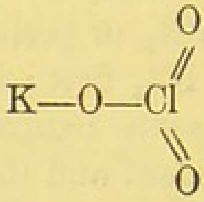
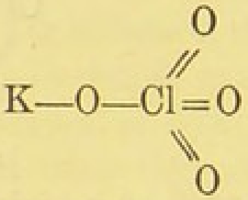
The consideration of such compounds as HIO_4 and $HClO_4$ will however serve to show that there are grounds for the belief that some elements possess a higher valency in molecules of a complex nature than they do in molecules of a simple nature. The series of compounds KCl, KClO, $KClO_2$, $KClO_3$, $KClO_4$ may be graphically written—

Potassium chloride	K—Cl
" hypochlorite	K—O—Cl
" chlorite	K—O—O—Cl
" chlorate	K—O—O—O—Cl
" perchlorate	K—O—O—O—O—Cl

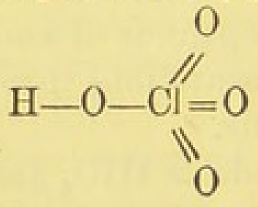
or thus[1] :—

---

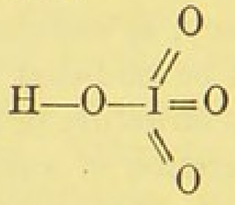
[1] A third alternative is based on the acceptance of the formulæ $K_2O.Cl_2O$, $K_2O.Cl_2O_3$, $K_2O.Cl_2O_5$, $K_2O.Cl_2O_7$.

Potassium chloride	$\mathrm{K{-}Cl}$
„ hypochlorite	$\mathrm{K{-}O{-}Cl}$
„ chlorite	$\mathrm{K{-}O{-}Cl{=}O}$
„ chlorate	 $\mathrm{K{-}O{-}\overset{O}{\underset{O}{Cl}}}$
„ perchlorate	 $\mathrm{K{-}O{-}\overset{O}{\underset{O}{Cl}}{=}O}$

Experience shows that where elements are linked together in series, the longer the series and the smaller is the stability of the compound, whereas $KClO_4$ is in reality more stable than $KClO_3$, and $KClO_3$ than $KClO_2$. This argument tells against the former method of representation, and for this reason, and also on other grounds, the second method is to be preferred. Hence we are led to accept the higher valency of chlorine and admit that, in potassium perchlorate, chlorine is heptavalent. Iodine under similar circumstances would be also heptavalent, and we should represent $HClO_4$ and HIO_4 graphically thus—



$\mathrm{H{-}O{-}\overset{O}{\underset{O}{Cl}}{=}O}$



$\mathrm{H{-}O{-}\overset{O}{\underset{O}{I}}{=}O}$

Prediction of elements and their properties.—There is always a very considerable resemblance in properties between a given element and the elements in the next line but one above and below it and also those immediately adjacent on the left and right of it. Approximately, the properties of the element are the mean of those of the four others which lie near it as described.

— M —
— — —
P X Q
— — —
— N —

If in the above scheme M N P Q are elements whose properties are already known, and X is an element not yet isolated, the atomic weight, atomic volume, valency, melting point and other properties of this element, and even the composition, stability and general character of its compounds, may be predicted.

In this way Mendelejeff predicted the properties of Eka-boron, Eka-aluminium and Eka-silicon, at that time unknown, but since isolated and called Scandium, Gallium and Germanium respectively. The correspondence between the properties as foretold and as realized is very close indeed. We see, then, that the periodic system is an aid towards the discovery of new elements, for it is able to foreshadow their properties and thus suggest the means to be adopted in their isolation.

CHAPTER III.

WATER, HYDROGEN PEROXIDE, OZONE, THE ATMOSPHERE.

Physical properties of water.—Water occurs not only in the liquid form, but also in the solid form, as ice or snow, and in the gaseous form, as water vapour or steam. Below 0° C. it takes the solid form, and above 100° C., at standard pressure,[1] it passes into steam; but at lower temperatures, however, water evaporates slowly into the air, and even in the solid condition, as snow and ice, evaporation goes on, though still more slowly. Water possesses a high specific heat, and is adopted as the unit with which other bodies are compared; ice has the specific heat 0·5, and steam 0·48.

Changes of volume of water at different temperatures.—When ice melts, the water which it forms is smaller in volume by nearly 10 per cent. than the ice from which it is formed. Also, as the temperature rises from 0 to 4° C. a further contraction, amounting however only to about $\frac{1}{100}$ per cent., occurs. At 4° C. water has its maximum density (and hence smallest volume), and above this it expands again as the temperature rises, until at 100° C. it occupies a volume rather over 4 per cent. greater than that at its maximum density. Water vapour has $\frac{1}{1240}$ the density of liquid water, and the volume of steam at 100° is nearly 1,700 times that of the water from which it is formed.

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[1] For further information concerning the tension of water-vapour and the boiling-point of water consult text-books on physics.

Latent heat of water and of steam.—When heat is imparted to ice it melts, but the thermometer continues to record 0° C. until the whole of the ice is melted, and when water is boiled the temperature of the water remains at 100° C., until it is wholly transformed into steam ; moreover, the steam resulting also shows the temperature of 100° C. Although heat is being continually imparted to the ice or water, as the case may be, the thermometer records no increment of temperature. This heat is termed *latent*, for although it is undoubtedly communicated to the ice or water, it is unrecognized by the thermometer. The following experiments will afford convincing evidence on this point.

If 100 c.c. of water at 0° C. are mixed with 100 c.c. of water at 80° C.* stirred quickly together, the temperature of the resulting 200 c.c. of water will be found to be 40° C. (or rather less, in point of fact, owing to radiation of heat during the experiment). If 100 grammes of snow or powdered ice are mixed with 100 c.c. of water at 80° C. ; the snow will just all melt, and the result will be 200 c.c. of water at 0° C.

In order to compare the results of these two experiments, we must adopt a unit of heat ; this is defined as that amount of heat which will raise one gramme of water 1° C. in temperature, and it is termed a *calorie*. Since in the former experiment we have as an end result 200 grammes of water at 40° C., and in the latter 200 grammes at 0° C., there is a difference of 8,000 calories in the results as recorded by the thermometer. This amount represents the *latent heat* of fusion of 100 grammes of water in the solid state (snow), and for one gramme the value would be 80. That is to say, that as much heat is needed to melt one gramme of ice or snow as would raise one gramme of water from 0° C. to 80° C.

This property is not peculiar to water, for, as a rule, when a change of physical condition occurs in any substance by the passage from the solid to the liquid state, similar phenomena can be observed. Frequent instances of it occur when salts, such as ammonium nitrate, calcium chloride, etc., are dissolved in water.

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* A simple form of calorimeter for this and similar experiments may be made of thin brass or copper standing on cork supports.

When the change takes place in the inverse manner, *i. e.* the passage from liquid to solid state, *heat is given out* equal in amount to that which, in the former case, had been rendered latent, and indeed the latent heat of steam is most readily ascertained by determining in this way the heat given out on the condensation of steam.

Similarly, the conversion of other liquids into vapour is accompanied by a large absorption of heat; a few drops of ether placed on the hand quickly evaporate and give rise to a sensation of great cold, the heat requisite for the transformation into vapour being abstracted from the hand.

And in general, whenever a change occurs in which the particles partake of a freer motion, heat really does disappear *as heat*, it being converted into energy of motion which is communicated to the particles.

So when the reverse change occurs, the energy of motion is converted back again into heat and reappears as such.

Freezing mixtures.—By dissolving a quantity of many salts such as ammonium nitrate or potassium iodide in water, a considerable depression of temperature may be obtained, but the freezing mixture most commonly employed is a mixture of common salt and snow or powdered ice, by which a temperature as low as − 23° C. may be reached.

The cooling is due to the fact that snow and salt when mixed, rapidly pass into the liquid condition, a change which we have seen is accompanied by an absorption of heat. The heat so absorbed in the passage from the solid to the liquid state is abstracted from the mixture, and hence the depression of temperature.

Any depression below − 23° C. would result in the separation of the solid cryohydrate $NaCl. 10\ H_2O$ (see page 67) with an *evolution* of heat which would counteract the cooling. The limit of temperature that can be attained by the use of salt and snow is therefore − 23° C.

Water as a solvent.—Most of the solid substances and gases which we meet with in chemical operations dissolve to an appreciable extent in water; some liquids, such as alcohol and sulphuric acid, associate themselves with water in all proportions; whilst others, such as oils, if shaken up with water separate again, being taken up by the water either only to a slight extent or not at all.

Solubility of solids.—The extent to which solid substances are soluble in water under similar circumstances varies according to the nature of the substance.

Minerals, such as coal, limestone, quartz, and many chemical compounds, such as sulphate of lime, oxide of lead, sulphide of iron, are only very slightly soluble, whilst others, *e. g.* nearly all chlorides and nitrates, are freely soluble. In any case, however, there is a limit to the amount of solid matter which can be dissolved, and when water has taken up as much as it will, we have what is known as a *saturated* solution.

The quantity of a substance required to form a saturated solution is usually greater the higher the temperature, though there is no simple general relation between the temperature and the amount dissolved.

The solubility in parts per 100 by weight of water is given for a few substances in the following table—

	0° C.	20° C.	50° C.	100° C.
Potassium nitrate ...	13·3	31·2	85·0	246·0
Sodium chloride ...	35·5	36·0	37·0	39·6
Potassium chlorate ...	3·3	8·0	19·0	58·0
Sodium chlorate ...	81·9	99·0	136·0	232·6
Mercuric chloride ...	5·7	7·4	11·3	54·0
Potassium sulphate ...	8·3	12·5	17·0	26·0

Solubility of gases.—There is no general connection between the solubility of gases and their chemical composition. Some gases, such as nitrogen, hydrogen, and carbon monoxide, are very slightly soluble, whilst others, such as ammonia, sulphur dioxide, and hydrochloric acid, are very freely soluble in water. The solubility, instead of increasing with the temperature, *decreases*, though in no simple relation. One volume of water at the temperatures stated, and under 760 m.m. pressure, dissolves the volumes of the respective gases given in the following table—

	0° C.	10° C.	20° C.
Nitrogen	0·020	0·016	0·014
Oxygen	0·041	0·033	0·028
Hydrogen	0·019	0·019	0·019
Carbon dioxide	1·799	1·185	0·901
Sulphuretted hydrogen ...	4·371	3·586	2·905

As instances of much more soluble gases we may take—

Sulphur dioxide	79·8	56·6	39·4
Hydrochloric acid ...	503·0	475·0	444·0
Ammonia	1049·6	812·8	654·0

The influence of pressure on the solubility of gases.—The volume of a gas which dissolves in water is directly proportional to the pressure (Henry's Law). Thus water at 0° C. dissolves of carbon dioxide—

At 1 atmosphere pressure 1·8 times its volume.
„ 2 atmospheres „ 3·6 „ „ „
„ 4 „ „ 7·2 „ „ „
„ ½ atmosphere „ 0·9 „ „ „
„ ⅓ „ „ 0·6 „ „ „

Soda-water is water charged with carbon dioxide under a pressure of about 4 atmospheres, and so long as this pressure on the surface of the water is maintained this volume of gas will be retained, but directly the pressure is released an effervescence is observed, and gas escapes from the liquid in proportion to the diminution of pressure.

Natural waters.—The water which evaporates from the surface of sea and land, and passes as water vapour into the air, is the purest form of natural water, and it retains its purity until it begins to fall as drops from the rain cloud.

Rain water.—When this is collected at the surface of the earth it has passed through a considerable stratum of air, and dissolved in its passage not only gases normally occurring in the atmosphere, but also such impurities as are found there. Even then the solid matter contained in it does not amount normally to more than 3 or 4 parts per 100,000. In the neighbourhood of towns the impurities taken up are more numerous and in larger quantity; also near the sea, and especially during high winds much sodium chloride is found in rain water.

River water.—The composition of this water will of course depend on the nature of the surface and of the strata over which the water passes. For instance, a considerable part of the drainage area of the Thames consists of chalk, and its water contains about 30 parts of dissolved matter in 100,000, two-thirds of this consisting of calcium carbonate and sulphate, whilst the Dee in Scotland, passing over the older strata (principally slate and sandstone), contains only 5·6 parts of dissolved matter per 100,000, one-fourth of this being calcium salts. Since the water which passes into rivers collects from the surface of the soil, it contains also much more organic matter and carbon dioxide than rain water, arising from contact with plants and decaying vegetable matter.

Spring water.—The water of springs is rain water which has percolated through soil and rocks. The composition of spring waters varies very considerably, according to the depth from which the water rises, and the nature of the strata which it has traversed. In some cases the amount of dissolved matter is very large, and such springs, especially when they have a saline taste or medicinal properties, are known as *mineral* springs.

The springs of Bath and Harrogate contain magnesia and sulphuretted hydrogen, and are known as magnesia and sulphur waters; a spring near Woodhall Spa contains free iodine; many springs contain iron, and are known as *chalybeate* waters.

Mineral springs which rise from great depths are frequently hot, some having a temperature of nearly 100° C.; this is especially the case in volcanic regions, where the earth's temperature rises more rapidly with increase in depth below the surface.

Spring water is bright and sparkling, since it is more fully charged with gases than either rain or river water, and contains less organic matter this being removed in its passage through beds of soil or gravel. The composition of some typical waters is given in the table further down.

Sea water.—The matters dissolved or suspended in river or spring water are carried to the sea and remain there, since the water vapour rising from the sea consists of practically pure water. So that notwithstanding the removal of large quantities of these impurities by settling out or by the action of organisms, sea water is still the most impure form of natural water, and owing to the large amount of matter in solution its specific gravity is on the average 1·03. In those land-locked seas which receive much river water the impurities are of course in smaller quantity, but in the open ocean the residue obtained on evaporating 100,000 parts of sea water amounts to about 3,600 parts, of which nearly four-fifths is sodium chloride, the rest being chiefly calcium and magnesium sulphate and magnesium chloride. The peculiar taste of sea water is due to the presence of these salts.

In the following table details are given of the composition of some typical natural waters, the solids in parts per 100,000, the gases in cubic centimetres per litre—

COMPOSITION OF SOME NATURAL WATERS.

	Solids.					Gases.		
	Total Residue.	Calcium Salts.	Magnesium Salts.	Sodium Chloride.	Organic Matter.	N.	O.	CO_2
Rain Water	3·4	*nil.*	*nil.*	0·5	1·0	13·1	6·4	1·3
River Water (Thames)	29	20	1·8	2·6	3·4	15·0	7·4	30·3
River Water (Dee)	5·6	1·4	0·5	1·0	2·2			
Spring Water	20			2·0	Traces	15·8		1·0
Mineral Water (Bath)	236	137	28	34	Traces	4·0	8·0	29·0
Sea Water	3,500	140	530	2,650	Traces	2·1	6·0	17·0

Chemically pure water may be obtained by distillation, the water being boiled and the steam which is given off condensed. On a small scale the apparatus shown (Fig. 6) may be used. The water is boiled in a flask connected with a condenser, through which a continual stream of cold water passes for the purpose of condensing the steam.

A small quantity of volatile organic matter may be carried over during a first distillation, and soluble matter from the glass condenser and receiver may be present: but on adding a few drops of potassium permanganate solution, and distilling again in platinum apparatus, very pure water is obtained.

Drinking water.—When water is to be used for drinking purposes, it is of the highest importance that it should be clear and colourless, and as free as possible from organic impurity arising from sewage contamination, or contact with decaying animal or vegetable matter. Dissolved salts, such as ordinarily occur in natural waters, are of less moment than organic impurity, and even such minute quantities as 0·3 or 0·4 per 100,000 may be injurious. The taste of drinking water is also an important factor, and whilst distilled water and rain water are flat and insipid, owing to the smaller quantity of dissolved gases which they contain, spring water has a characteristic freshness which renders it most palatable.

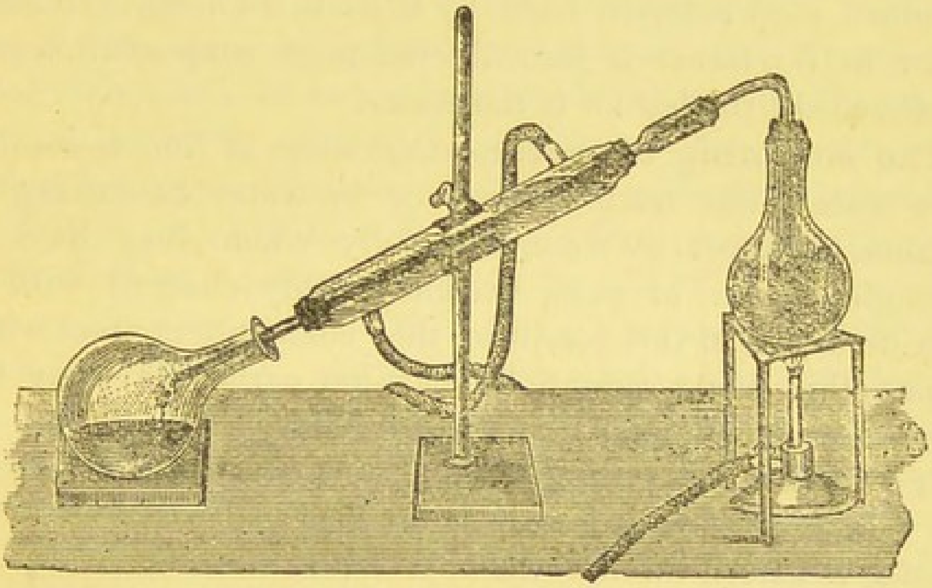

FIG. 6

Hardness of water.—It is a matter of common experience that the sensation felt when washing the hands differs with waters from different sources. With rain water or the waters derived from sandstone areas a lather quickly forms, whilst with calcareous waters there is a sense of harshness, and a good deal of soap is required to produce a lather; we notice further that in the latter case a scum is formed which floats on the surface of the water. Waters that readily form a lather are known as *soft* waters, whilst those which do not are called *hard* waters. Hard waters contain much dissolved matter, and especially salts of lime or magnesia, which are the chief cause of the hardness.

The cleansing action of soap is due to the alkali and fatty acids which it contains, and no lather begins to be produced—or in other words no soap is available for cleansing—until the whole of the lime or magnesia in the water has entered into combination with the fatty acids to form the scum of which we have spoken. The hardness of any sample of water is indeed measured by adding a standard soap solution little by little to a known volume of the water until a lather is formed; the more soap solution required to effect this, the harder is the water.

The softening of water.—Carbonate of lime is insoluble in pure water, but readily dissolves in water containing carbon dioxide. Natural waters, especially when they have passed through a layer of peat, become highly charged with carbon dioxide, and if in this condition they come into contact with limestone (this being essentially calcium carbonate) they take up calcium carbonate and are rendered hard.

If to a few cubic centimetres of lime water four or five times the volume of distilled water are added and a stream of carbon dioxide is passed through the clear liquid. At first a turbidity is produced, owing to the formation of calcium carbonate—

$$CaO + CO_2 = CaCO_3.$$

But on continuing to pass the gas the liquid will become quite clear again, because we have now carbon dioxide in solution in the water. If the clear liquid is divided into two portions, and one portion is boiled for a little time and to the other a volume of lime water equal to that originally taken is added. In each case the turbidity first noticed will be reproduced, since we have got rid of the excess of carbon dioxide; in the first case we expelled the excess of carbon dioxide by heat, in the second we added sufficient lime to combine with it and form calcium carbonate.

We may, then, precipitate the calcium carbonate and get rid of the hardness due to this cause, (*a*) by boiling the water, (*b*) by adding to it the proper amount of lime (Clark's process), and after allowing the precipitate to settle the water will be found to yield a lather with less soap than before: it has become softer. Hardness due to calcium and magnesium carbonates can be removed in this way, and is termed *temporary hardness.* The hardness due to sulphates and chlorides of lime, magnesia, etc., cannot, however, be got rid of by boiling, and is known as *permanent hardness.* Boiling water in a kettle or steam boiler therefore makes it softer, and the "fur" which forms on the vessel is chiefly calcium carbonate which has been precipitated during the process.

Water of crystallization. — Many salts, when they are allowed to crystallize from solution, contain water, which is associated with them in definite proportions, and it cannot be regarded otherwise than as water *in combination* with the salt.

There is, however, very little stability in the combination; for instance, copper sulphate crystallizes with the composition $CuSO_4.\ 5\ H_2O$. At 100° C. 4 H_2O is set free, and the remaining molecule of water requires a temperature of 240° C. to liberate it.

Alum crystallizes with 24 H_2O, 10 H_2O separate at 100° C., a further 9 H_2O at 120° C., and nearly the whole of the remainder at 280° C. In some cases, indeed, such as crystallized sodium carbonate or washing soda, $Na_2CO_3.\ 10\ H_2O$, the salt loses water or *effloresces* at ordinary temperatures in a dry atmosphere.

The amount of water of crystallization which attaches itself to a salt varies according to the temperature at which the crystals form. Thus, from a solution of sodium sulphate, crystals of $Na_2SO_4.\ 7\ H_2O$ can be obtained at temperatures below 26°, or crystals of $Na_2SO_4.\ 10\ H_2O$ (Glauber's salt) at temperatures below 34°: while above 34° crystals of Na_2SO_4 are obtained. Epsom salts $MgSO_4.\ 7\ H_2O$ furnishes another example giving $MgSO_4.\ 6\ H_2O$. Frequently, salts which at ordinary temperatures separate from solution in the anhydrous condition, possess water of crystallization when crystallized at low temperatures. Thus if a concentrated solution of common salt be allowed to stand at ordinary temperatures crystals of NaCl are obtained, but at - 10° C. crystals of $NaCl.\ 2\ H_2O$, and at - 23° C. crystals of $NaCl.\ 10\ H_2O$ separate: compounds like the two last are called *cryohydrates.*

Composition of water by volume.—The method employed at the present day, which we owe to Bunsen, is similar in principle to that employed by Cavendish in 1781, but capable of greater accuracy, and is moreover applicable to gases in general.

A tube of even bore, about 700 millimetres in length, is used.

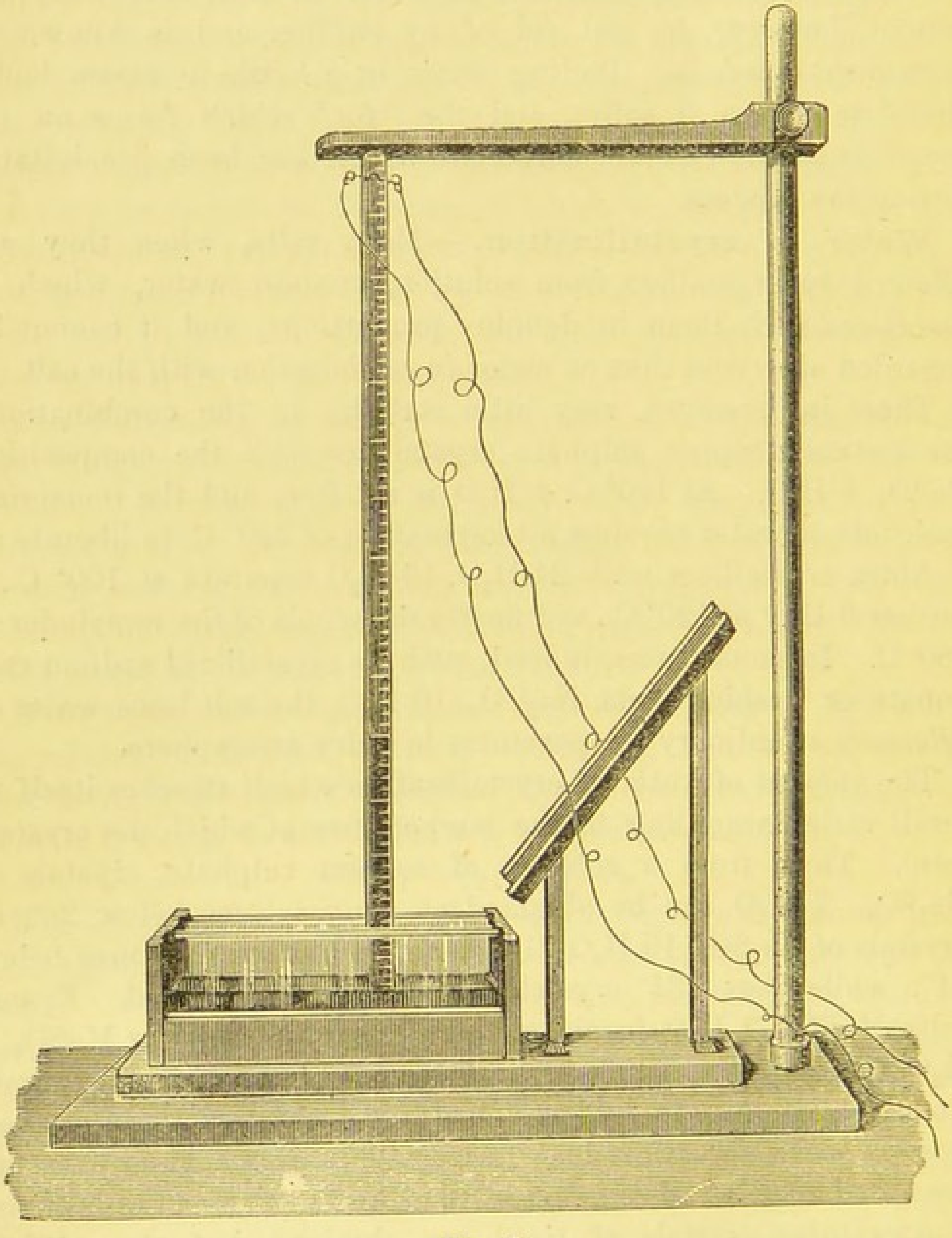

Fig. 7.

This is furnished with platinum wires to enable the gases to be "sparked," and millimetre divisions are etched on the tube. The "eudiometer," as such a tube is called, is first calibrated so that its relative volume down to any given graduation is known. It is then moistened on the inside with a few drops of water, filled with mercury and inverted in a trough containing mercury. Pure oxygen sufficient to occupy about one-tenth of the volume of the eudiometer is now passed in, and the exact level of the mercury in the eudiometer and in the trough is read. Hydrogen is then added equal to about six or seven times the volume of the oxygen, and the levels of the mercury again read. The temperature and pressure existing at the time must also be noted. The eudiometer is now closed by pressing it down firmly on an india-rubber cushion at the bottom of the trough, and the spark is passed.

Under these circumstances the whole of the oxygen enters into combination with hydrogen, and as the water which forms condenses, a partial vacuum is formed inside the tube, and on gently raising it from the cushion the mercury is seen to rise. After allowing sufficient time for the gas to regain the temperature of the room (much heat having been generated by the combination which has taken place) the levels of the mercury in the eudiometer and trough are again read.

We have now the whole of the data necessary for ascertaining the relative volumes of hydrogen and oxygen which have united to form water. The volumes occupied by the gases are all reduced so as to represent standard conditions, and correction is made for the tension of aqueous vapour.[1] When this has been done, let us suppose—

Oxygen taken occupied 12 volumes.
Hydrogen added ,, 80 ,,
Residual hydrogen ,, 56 ,,

---

[1] If a tube closed at one end and open at the other, and about one metre in length, be completely filled with mercury and inverted over a vessel containing mercury, the mercury will fall in the tube until the difference in level between the mercury in the trough and in the tube is about 760 m.m. If a few drops of water are now allowed to rise through the mercury into the vacuous space above it, part of the water will be vaporized and cause a depression of the mercury in the tube. This is because the water vapour exerts a pressure. This pressure is called the tension of aqueous vapour, and has a particular value at each particular temperature. Hence, in the case in point, the pressure on the gas will be the total pressure as calculated from the levels, less the tension of aqueous vapour.

It is evident that 12 volumes of oxygen have entered into combination with 24 volumes of hydrogen to form water.

If we arrange to surround the eudiometer with a steam-jacket, so as to prevent the condensation of the water, we shall be able to ascertain that the volume of the water vapour produced is exactly that of the hydrogen it contains. We may summarize these facts in the statement—*Two volumes of hydrogen combine with one volume of oxygen to form two volumes of water vapour or steam.*

Cavendish in 1781 was the first to ascertain the composition of water. He introduced a mixture of two volumes of hydrogen and one of oxygen into a strong glass vessel fitted with two wires, which passed into the inside of the vessel so as nearly to touch one another. The electric spark was passed by means of the wires, and the gases exploded. By repeating the experiment many times, he was able to show that oxygen combines with twice its volume of hydrogen, and that the liquid resulting from the combination was water.

Composition of water by weight.—Many oxides, such as those of lead, copper, iron, etc., when heated in a current of hydrogen give up their oxygen, and are "reduced," as it is termed, to the metallic condition. In this reduction the oxygen combines with hydrogen with the production of water. If, then, we can ascertain (1) the weight of the water formed, and (2) the weight of the oxygen which has gone to form it, we shall have by difference the weight of the hydrogen contained in the water, and thus a full synthesis of water by weight. Very careful experiments have been performed in this way, using oxide of copper (CuO) as the medium for the supply of the oxygen. The equation expressing the reaction is—

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

Our requirements for the performance of the synthesis are—

(1) Pure hydrogen.

(2) A known weight of oxide of copper.

(3) A means of collecting and weighing the *whole* of the water produced.

Dumas and Stas, in 1843, performed the synthesis of water in this way with extreme care, and the requirements above-mentioned were attained in the following manner. The hydrogen, prepared by the action of zinc on sulphuric acid, was purified by passing it through nitrate of lead, sulphate of silver, and caustic potash, and then carefully drying it by passing it over phosphorus pentoxide. The oxide of copper was placed in a bulb A, the weight of both being determined. The greater part of the water condensed in the bulb B, and the rest was absorbed in U tubes containing solid caustic potash C and phosphorus pentoxide D.

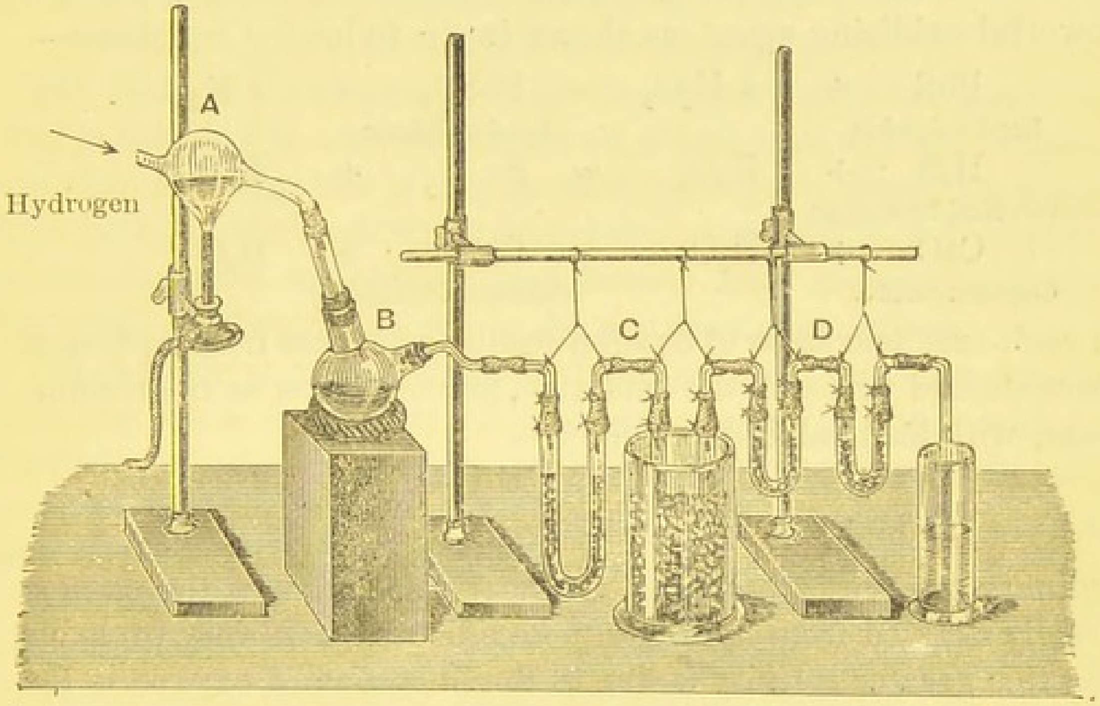

FIG. 8.

Weighings before and after the experiment show—

(*a*) The loss of weight of the oxide of copper, that is, the amount of oxygen used ;

(*b*) The gain in weight of the second bulb B and the U tubes succeeding it, that is, the amount of water formed. As the combined result of nineteen determinations, they found that the amount of oxygen used was 840·161 grammes and the amount of water formed 945·439 grammes. Water consists, therefore, of

840·161 grammes of oxygen
and 105·278 ,, ,, hydrogen ;

or one part by weight of hydrogen combines with 7·98 parts of oxygen to form water.

HYDROGEN PEROXIDE.—Hydrogen occurs in combination with oxygen, not only in the proportion represented by H_2O (as water), but also in that represented by H_2O_2 (hydrogen dioxide or peroxide), which contains twice as much oxygen, in relation to hydrogen, as water does.

This substance has been found in very small quantities in rain and snow, and also in the water formed by the combustion of hydrogen. It is a very unstable body, and readily undergoes decomposition into water and oxygen; it bleaches vegetable colours, and is a powerful oxidizing agent, as shown in the following equations—

$$\underset{\text{Lead sulphide.}}{PbS} + 4\,H_2O_2 = \underset{\text{Lead sulphate.}}{PbSO_4} + 4\,H_2O$$

$$\underset{\text{Sulphuretted hydrogen.}}{H_2S} + H_2O_2 = S + 2\,H_2O$$

$$\underset{\text{Calcium oxide.}}{CaO} + H_2O_2 = \underset{\text{Calcium dioxide.}}{CaO_2} + H_2O$$

In each case one atom of oxygen readily separates from hydrogen peroxide and performs the oxidation, leaving water as the residue. Thus, with lead sulphide we have—

$$4\,H_2O_2 = 4\,H_2O + 2\,O_2$$
$$\text{and } PbS + 2\,O_2 = PbSO_4.$$

Ordinary oxygen is, however, not nearly so active as the oxygen directly derived from hydrogen peroxide, and it is very probable that this greater activity is due to the liberation of oxygen in the atomic condition, so that the reaction would be—

$$4\,H_2O_2 = 4\,(H_2O + O)$$
$$\text{and } PbS + 4\,O = PbSO_4.$$

This is the more likely since, in presence of hydrogen peroxide certain oxides are deprived of oxygen; thus—

$$Ag_2O + H_2O_2 = 2\,Ag + H_2O + O_2.$$

In such cases there is a single atom of oxygen feebly attached in *both* compounds, and these are readily liberated and combine to form the molecule of oxygen—

$$Ag_2 \mid O + O \mid OH_2.$$

Hydrogen peroxide can be preserved in dilute solution, and is so prepared by the action of dilute acids on barium peroxide—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

In order to prepare hydrogen dioxide 10 c.c. of concentrated sulphuric acid are added to 200 c.c. of water, and the mixture is allowed to stand till it becomes quite cold; then little by little, with constant stirring, about 30 grammes of barium peroxide are added. The $BaSO_4$ is allowed to settle and the clear liquid is poured off. It is a dilute solution of hydrogen peroxide, and the following experiments may be performed with it—

(1) To some of the liquid add potassium iodide, iodine will be liberated, and the solution become brown—

$$2\ KI + H_2O_2 = KOH + I_2.$$

(2) Make a dark stain of sulphide of lead on filter paper by first moistening it with a solution of a lead salt, say the acetate, and then exposing this to sulphuretted hydrogen. Steep the paper in a little of the hydrogen peroxide solution and it will become white, the black sulphide of lead having been transformed into the white sulphate, as shown in the equation given above.

(3) Add silver nitrate to some of the solution, and then caustic soda; a black precipitate of hydrated oxide of silver will be formed, and this in contact with the hydrogen peroxide will undergo decomposition in the manner already described; the effervescence of gas which occurs is due to oxygen.

A concentrated solution of pure hydrogen peroxide may be obtained from the dilute solution by careful distillation, the operation being performed under diminished pressure.

Manganese dioxide, like silver oxide, decomposes hydrogen peroxide with the evolution of oxygen, but in this case *if there be no acid present* the oxide of manganese is not itself reduced:

$$MnO_2 + 2\ H_2O_2 = MnO_2 + 2\ H_2O + O_2.$$

If acid be present both the oxides are reduced and the manganous oxide (MnO) formed dissolves in the acid forming a salt:

$$MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2\ H_2O + O_2.$$

Potassium permanganate behaves similarly, MnO_2 being formed in a neutral solution and $MnSO_4$ in an acid solution.

$$2\ KMnO_4 + H_2O_2 = 2\ MnO_2 + 2\ KOH + 2\ O_2.$$

$$2\ KMnO_4 + 4\ H_2SO_4 + 5\ H_2O_2 = 2\ KHSO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ O_2.$$

Bleaching powder in presence of H_2O_2 likewise yields oxygen:

$$Ca < {Cl \atop OCl} + H_2O_2 = CaCl_2 + H_2O + O_2.$$

OZONE.—Under certain conditions oxygen is found to possess a peculiar odour, similar to that observed in the neighbourhood of an electrical machine during electrical discharge ; and it differs from ordinary oxygen in its physical and chemical properties. This modified form of oxygen is termed ozone. Under no circumstances has it been found possible to obtain ozone in the pure state, as even under the most favourable conditions only about 8 to 10 per cent. of the oxygen is transformed into ozone, the remainder being oxygen in the ordinary form ; usually, indeed, the proportion of ozone is much smaller.

Preparation of Ozonized Oxygen.—Ozone occurs in the oxygen produced during the electrolysis of water, but is most conveniently obtained by passing an electric discharge from two Grove's cells and an induction coil, through dry oxygen. For this purpose the apparatus shown (Fig. 9) may be used. An outer tube A B ending below in a narrower portion bent into a U-tube, is provided with two stop-cocks, and an inner tube of somewhat smaller diameter, closed at the bottom, and sealed in at A. The outer tube is surrounded throughout its whole length by a coil of platinum wire, and the inner tube is filled with dilute sulphuric acid, and another platinum wire dips into this. The stop-cocks are opened, and concentrated sulphuric acid is poured into the U-tube, which serves as a gauge,

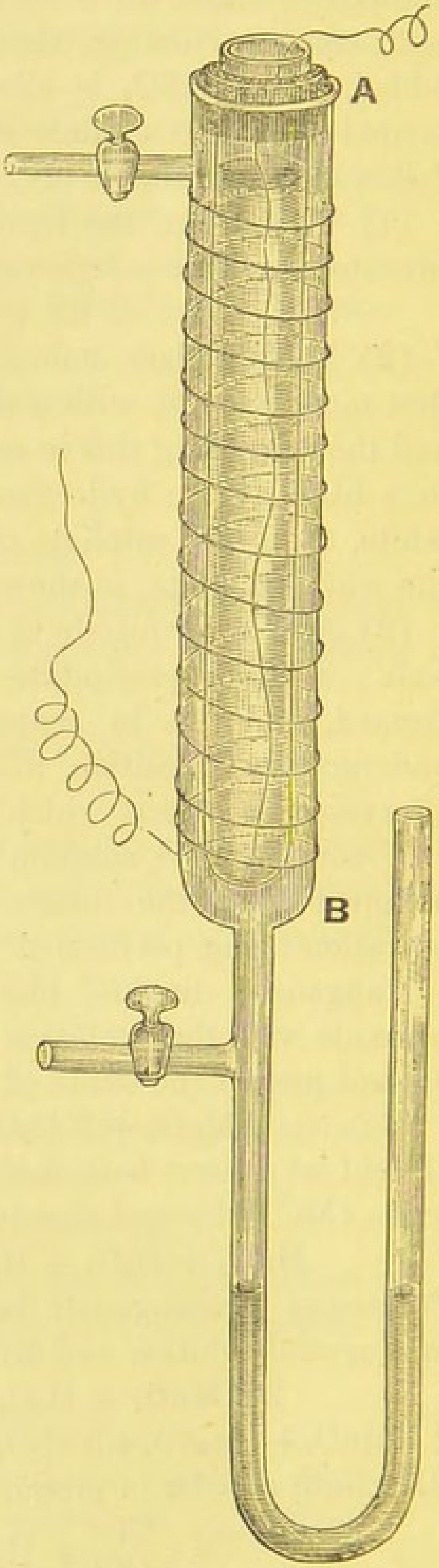

FIG. 9.

and dry oxygen passed through the annular space till the air is swept out. Now close the stop-cocks and connect the two platinum wires to the terminals of the induction coil. The temperature of the apparatus should be kept constant during the experiment, and this may easily be effected by surrounding it with water at the same temperature as the room. After passing the current for a little while, some of the oxygen contained in the space between the tubes will have been converted into ozone, and the following observations may be made.

(1) The volume of the gas in the annular space diminishes, as will be indicated by the sulphuric acid in the gauge. By determining beforehand the relative volume of the space in which the oxygen is confined, and that of a given length of the U tube, an approximate estimate may be made of the amount of contraction.

(2) Attach a tube at the upper stop-cock, open both stop-cocks, and drive out some of the ozonized oxygen at the lower one, holding a paper dipped in solution of potassium iodide near the outlet. The paper will turn brown from the liberation of iodine, the ozone being transformed into ordinary oxygen.

$$2\,KI + O_3 + H_2O = 2\,KOH + O_2 + I_2.$$

(3) Bleach indigo or moist litmus in a similar way.

(4) Note the odour of the ozone.

(5) Put a globule or two of mercury in a small flask and pass ozonized oxygen into the flask. On shaking, the mercury is superficially oxidized, loses its convexity of surface, and spreads out in a film on the walls of the flask.

(6) Expel the ozonized oxygen from the lower stop-cock through a glass tube about 20 cms. long, heating the tube to dull redness; at 250° C. ozone is transformed into oxygen, and after heating, a test made as in (2) should give no liberation of iodine.

The above observations show the great chemical activity of ozone, and the features by which it is distinguished from oxygen, for ordinary oxygen does not bleach, nor does it oxidize mercury or liberate iodine from potassium iodide at ordinary temperatures; it may be added that ozone is readily taken up by turpentine and certain essential oils. Ozone occurs in the atmosphere in minute quantities, except in those districts where the air is considerably polluted by smoke or organic matter.

Composition of ozone.—That ozone is oxygen in a condensed form appears from the fact that it is formed from pure oxygen, and that when oxygen is transformed into ozone a contraction in volume takes place. This contraction may be measured; let us suppose that in a given experiment it amounted to 3 per cent. of the total volume of the gas originally taken—that is, 100 volumes of gas have been contracted to 97 volumes.

If we now absorb the ozone by means of turpentine, we shall find a further diminution in volume, and the oxygen which remains will be found to occupy 91 volumes. We have, then—

Volume of ozone ... ... = (97 − 91 vols.) = 6 vols.
,, ,, oxygen from which it was formed = (100 − 91 vols.) = 9 vols.

The ozone was therefore formed by the condensation of 9 volumes of oxygen into the space of 6 volumes, or 3 volumes of oxygen condense to produce 2 volumes of ozone.

Expressed by means of symbols—

$$3\ O_2 = 2\ O_3.$$

Ozone has therefore $1\frac{1}{2}$ times the density of oxygen, *i. e.* 24.

This result has been checked by observing the rate of diffusion of ozone. When gases diffuse through a porous membrane, such as a plate of plaster of Paris, it is found that the lighter the gas the more rapidly does it pass through the membrane, and accurate measurements show that *the comparative rate of diffusion of two gases is inversely as the square root of their densities.*

Thus the densities of H and O are 1 : 16.

The square root of these densities is 1 : 4.

Hydrogen therefore diffuses through a porous membrane four times as fast as oxygen.

The comparative rate of diffusion of ozonized oxygen and chlorine has been measured, and the results indicate that—

Rate of diffusion of Cl : Rate of diffusion of ozone approximately : : 5 : 6.

Thus density of Cl : density of ozone approximately as $6^2 : 5^2$, or 36 : 25.

The actual density of chlorine is 35·4, and hence we must conclude that the actual density of ozone is in agreement with the value based on the acceptance of O_3 as representing a molecule of ozone, and occupying the space of a molecule of hydrogen, H_2.

THE ATMOSPHERE.—The gaseous envelope which surrounds the earth is chiefly composed of nitrogen and oxygen. With these are associated water vapour, carbon dioxide, ammonia, and other gases, the amounts of which vary according to circumstances. From whatever locality the air has been obtained, the relative proportions of nitrogen and oxygen show only slight variations, as the following results show.

Percentage of Oxygen by Volume.

72	analyses in different parts of Europe	(mean)	20·95
17	,, ,, the Polar Seas	,,	20·90
3	,, at elevation of 15,000 ft. or over	,,	20·94

The determination of the composition of the atmosphere.—If a known volume of air, from which the impurities have been removed, be introduced into a eudiometer and exploded with about twice its volume of hydrogen (see p. 68), two volumes of hydrogen combine with one volume of oxygen to form water vapour, which condenses, and thus *one-third* the diminution in volume represents the volume of oxygen present.

The difference between this and the original volume of air taken is the volume of nitrogen.

An approximate determination of the composition by volume may be made in the following way. Take a glass tube about 700 m.m. high and 15 m.m. diameter closed at one end, and of as even bore as possible. Invert this, filled with air, over water, note the volume of the air, and pass up into it a piece of phosphorus attached to a stout copper wire. The phosphorus will slowly combine with the oxygen of the air, and the water will rise in the tube. Allow it to stand in a shaded place until the water ceases to rise. Now remove the phosphorus, and adjust the level of the water to the same height inside and outside the tube, and note the volume of residual nitrogen. The volume (correction may have to be made for variation of temperature and pressure during the experiment) occupied by the original air and the residual nitrogen may be ascertained with tolerable accuracy by seeing what volume of water is required to fill the tube to the two levels noted.

The composition of air by *weight* may be ascertained by passing the air over red-hot copper, with which the oxygen

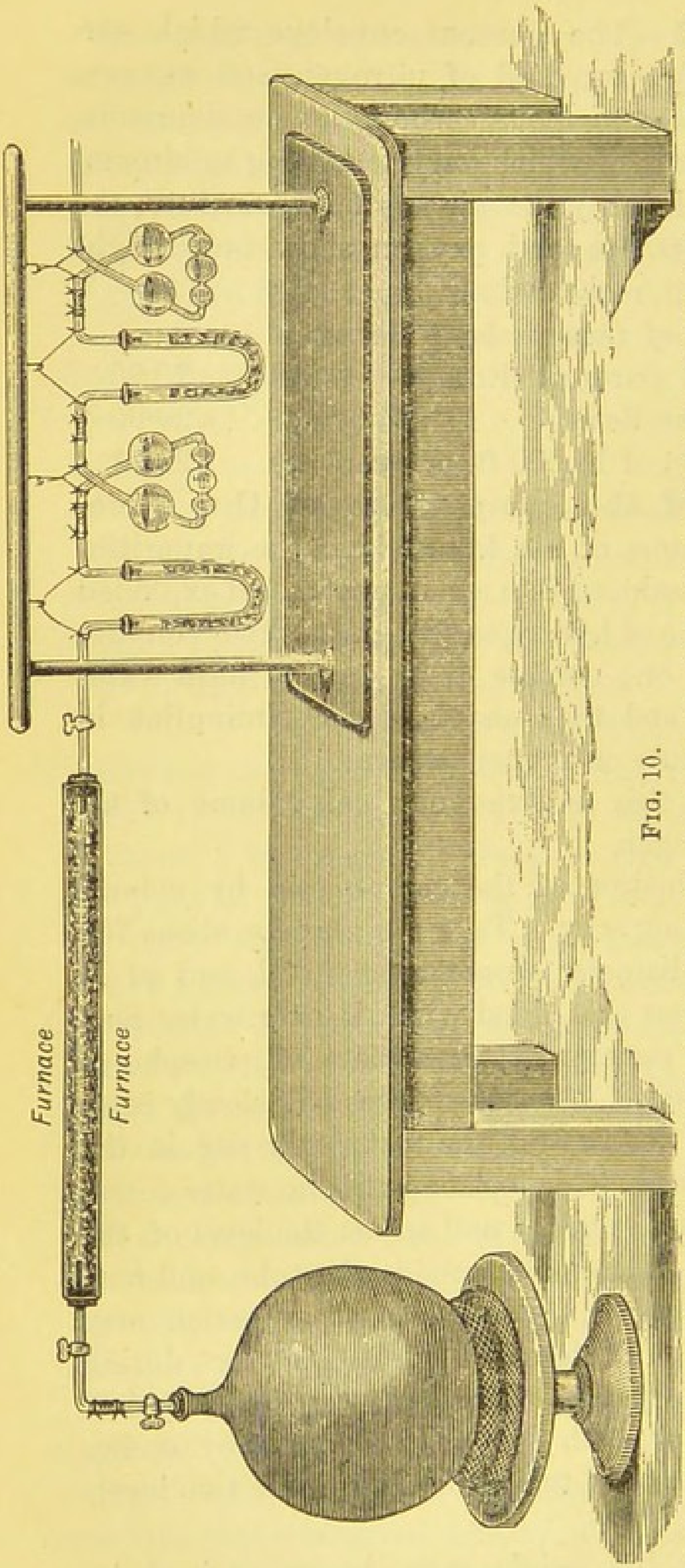

FIG. 10.

combines to form copper oxide. The air is previously freed from carbon dioxide and moisture, by being passed over potash and concentrated sulphuric acid. The apparatus used is shown in Fig. 10; it consists essentially of a large glass globe, to which is attached a tube containing metallic copper, and heated in a furnace. The globe is first rendered vacuous by means of a good air-pump, the stop-cock is closed, and the globe carefully weighed. The tube containing the copper is then rendered vacuous, closed and weighed. The copper having been heated to redness, the stop-cock is opened sufficiently to allow a slow current of purified air to pass through the tube and into the glass globe. On the way, it is deprived of its oxygen, and if the experiment has been carefully conducted, only nitrogen passes into the globe. After the apparatus has quite cooled, the globe is again weighed, and the increment gives *the weight of the nitrogen.* The tube is also weighed again, and the increase there shows *the* *weight of the oxygen*, together with a little nitrogen which remains in the tube. On exhausting and weighing again, the decrease in weight is added to the increase in weight of the globe to obtain the total nitrogen. The oxygen is given by the difference of the two weighings of the *exhausted* tube.

A series of such determinations gave the composition by weight of air as—

Nitrogen	76·995
Oxygen	23·005

Water vapour in air.—The amount of water vapour varies with the temperature and the degree of saturation of the air, for the higher the temperature of the air, the more moisture will it take up before it is saturated. The average amount is somewhat under 1 per cent. by volume, but in warm, moist climates may approach 4 per cent. It may be measured by observations on the dew-point (see text-books on physics), or by passing a known volume of air over calcium chloride contained in U tubes, and noting the increase in weight of the tubes.

The amount of water vapour which the air can contain may be estimated by the fact that 1 cubic mile of air saturated at 35° would deposit, if cooled to 0°, 140,000 tons of rain. But while the air is seldom completely saturated, it never contains less than $\frac{1}{10}$ of the possible amount.

Carbon dioxide in air.—The amount of this gas in air varies considerably, according to the locality from which the sample of air is taken. In country air there are from three to four volumes of CO_2 in 10,000, but in towns the amount is larger, and may reach seven or eight volumes. In badly-ventilated dwellings even ten-fold the normal amount of carbon dioxide may occur. The determination of carbon dioxide is a matter of importance, especially in the case of indoor air, since it serves to show the efficiency of ventilation.

The presence of carbon dioxide in air may be shown by exposing lime-water in a shallow dish; the lime-water is soon covered with a thin pellicle, owing to the formation of calcium carbonate or chalk, which is insoluble in water—

$$CaO + CO_2 = CaCO_3.$$

Baryta water may, by Pettenkofer's method, be used as a means of determining the amount of carbon dioxide in air. A solution of baryta (which is alkaline) of known strength is shaken up with a measured quantity of air, say 10 litres; part of the baryta is converted into barium carbonate (a neutral body), whilst part remains unaltered. The amount of alkali (the baryta) is now smaller by reason of the conversion of part of it into carbonate by the carbon dioxide. The more carbon dioxide is present, the greater will be the amount of baryta converted into barium carbonate, and the greater will be the difference between the amount of alkali originally taken and that remaining afterwards. By ascertaining the amount of oxalic acid required to neutralize the original baryta water, and that required to neutralize the residual liquid, the quantity of carbon dioxide in the 10 litres of air may be ascertained.

Other impurities in air.—The remaining impurities, such as suspended dust and carbon, ammonia, sulphur compounds, hydrochloric acid and chlorides, occur in much smaller and more variable quantities. During thunderstorms oxides of nitrogen are formed, and these give rise to nitrous and nitric acid; ozone is also probably produced under such circumstances. The ammonia, carbon (soot), and sulphur compounds occur in larger quantity in the vicinity of towns, from the combustion of coal, or where decaying refuse is found. The hydrochloric acid and chlorides come for the most part from manufacturing operations, though it is significant that, especially during high wind, the air in the neighbourhood of the sea contains much more sodium chloride than is usual.

The relation of animal and plant life to air.—By breathing on a cool glass surface, and by expelling air from the lungs through lime-water, it is easy to demonstrate that expired air contains large quantities of moisture and carbon dioxide. Indeed the expired air from man contains usually over 4 per cent. of carbon dioxide, that is, over one hundred times as much as normal air.

The agencies at work in producing carbon dioxide are—

(1) Respiration of animals and plants.
(2) Combustion of fuel.
(3) Decay of organic matter.
(4) Subterranean causes.

Faraday calculated that nearly five million tons of carbon dioxide were contributed daily to the atmosphere by these processes. Under such a contribution the air would slowly get more and more charged with carbon dioxide, and the percentage of oxygen diminish.

There are, however, processes constantly in operation which act in the opposite direction.

(1) In the process of assimilation the green colouring matter of plants (chlorophyll), in presence of direct or diffused sunlight, effects the decomposition of carbon dioxide and liberates oxygen.

(2) Carbon dioxide being moderately soluble in water is carried down by rain, and is also taken up by surface waters and sea water.

The precise extent to which the loss and gain counteract one another is difficult to estimate, but that plant life is an important factor is shown by actual observations on the living plant, and by the variations in the amount of carbon dioxide in air in the neighbourhood of forests in the daytime, when the foliage is exposed to the sun's rays, as compared with night, when assimilation is checked and only respiration goes on.

Is air a compound or a mixture of nitrogen and oxygen?—We have seen that a chemical compound shows the following characters—

(1) It possesses a *definite* composition.

(2) The weights of the elements composing it are in proportion to the atomic weights, or in some simple multiple proportion of the atomic weights—*e.g.* HgI, HgI_2, H_2O, etc.

(3) The compound shows distinctive physical and chemical properties, the individual properties of the constituent elements being more or less completely concealed.

(4) When combination takes place, heat is usually evolved.

(5) When gases combine to form a gaseous compound there is always a condensation to *two volumes*, whatever the volumes of the constituent gases may be, thus—

2 vols. hydrogen + 1 vol. of oxygen form 2 vols. water vapour.
3 ,, ,, + 1 ,, nitrogen ,, ,, ammonia.

(6) The simple solution of a gas in water does not affect its

chemical composition; for instance, if we dissolve ammonia or carbon dioxide in water, and then, by boiling the solution, expel the gas again, it will be found to be unaltered in character or composition.

Now let us apply these tests to air.

(1) The composition of air varies very little under different circumstances, but even such small variations as are found in its composition do not occur in the case of chemical compounds.

(2) If we divide the relative proportions by weight of nitrogen and oxygen in the air by the atomic weights of nitrogen and oxygen, we shall see whether any simple multiple relation is shown.

$$\text{Nitrogen } \frac{76{\cdot}995}{14} = 5{\cdot}499\,;$$

$$\text{Oxygen } \frac{23{\cdot}005}{15{\cdot}96} = 1{\cdot}441\,;$$

$$\text{And } 5{\cdot}499 : 1{\cdot}441 :: 3{\cdot}82 : 1.$$

That is, to be even approximately in agreement with the results of analysis we should have to assume a compound $N_{19}O_5$. The same result may be arrived at by considering the volume relations of nitrogen and oxygen in air.

(3), (4), and (5) Nitrogen and oxygen retain their characters with slight modification in air, and a mixture of the two gases in the proper proportions shows precisely the same characters in all respects as air. No heat is evolved when they are brought together, nor does any contraction in volume take place.

(6) It has been found that when air is shaken up with water, a greater proportion of oxygen dissolves than nitrogen, owing to the greater degree of solubility of oxygen, so that whilst in the air originally taken, one volume of oxygen is associated with approximately four volumes of nitrogen, air dissolved in water consists of one volume of oxygen associated with two volumes of nitrogen.

On all these grounds, therefore, we must admit that air is simply a *mixture* of nitrogen and oxygen.

Fogs are caused by condensation of water vapour induced by dust. That dust is the cause of fog formation is proved by the fact that in filtered air fogs cannot form. Analysis of the deposit left after a fog showed it to consist of carbon, hydrocarbons, sulphuric acid, iron and its oxides, and silica. During a fog, too, the amount of carbon dioxide increases enormously and reaches from three to five time the normal amount.

Manufacture of oxygen from atmospheric air.—From time to time processes have been tried for separating the nitrogen and oxygen of the air and obtaining oxygen on a large scale. One or two of these may be mentioned.

(1) If cuprous chloride be exposed to moist air at ordinary temperatures, it takes up oxygen and is converted into the oxychloride

$$2\,Cu_2Cl_2 + O_2 = 2\,CuOCl_2$$

and if this oxychloride be heated to dull redness it sets free the oxygen and is again transformed into cuprous chloride.

$$2\,CuOCl_2 \text{ by heat} = 2\,Cu_2Cl_2 + O_2.$$

(2) A mixture of lead oxide (PbO) and chalk ($CaCO_3$) if heated to dull redness in air forms calcium plumbate (Ca_2PbO_4). This is a compound of lead peroxide (PbO_2) and by liberating the PbO_2 by treatment with a solution of sodium carbonate, drying it and then heating it, oxygen is liberated.

$$2\,PbO_2 = 2\,PbO + O_2.$$

(3) A method which has, however, now been carried into practice on a large scale for some years and yields a continuous supply of oxygen very cheaply is the Brin process. This is based on the fact that if baryta (BaO) be heated to dull redness in air, it takes up oxygen and is converted into the peroxide (BaO_2); if now this be exposed to a still higher temperature, the oxygen taken up is set free and baryta left.

$$2\,BaO_2 = 2\,BaO + O_2.$$

The original proposition of Boussingault to prepare oxygen on the large scale in this way failed owing to certain difficulties. These were, however, finally overcome by the Brin process. In this process the same reaction was made use of, but it was found that in order to make the process a continuous one, the following conditions must be attended to:—

(*a*) the air must be freed from CO_2 and excessive moisture.

(*b*) the baryta must be so prepared as to obtain it into a firm and yet porous condition. It is obtained in the best condition by heating barium nitrate.

(*c*) the temperatures employed in the oxidation of the baryta and its subsequent deoxidation must be kept as low as possible.

An important modification of the original process has also been made under which it is no longer necessary to work alternately at higher and lower temperatures. By means of a force pump, the air is brought into contact with the heated baryta under a pressure of about 15 lbs. to the square inch. When sufficient time has elapsed to allow of conversion into barium peroxide connection is made with an exhaust pump, and the pressure reduced to about one-tenth of an atmosphere. Under so low a pressure the barium peroxide is decomposed at the same temperature which under higher pressures sufficed to form it. Instead, therefore, of varying the temperatures it is only necessary to establish high and low pressure alternately, the periods of operation being about a quarter of an hour.

The baryta is contained in a number of iron cylinders connected together by pipes and placed vertically in a furnace and heated by "producer gas" The working is practically continuous and only needs to be interrupted about every six months for the purpose of breaking up the baryta and adding a little fresh material.

CHAPTER IV.

THE MANUFACTURE OF THE MINERAL ACIDS.

NITRIC ACID OR AQUA FORTIS HNO_3.—This acid is obtained on the large scale by acting on Chili saltpetre ($NaNO_3$) with sulphuric acid of the specific gravity 1·7 (*i.e.*, acid containing ¼ its weight of water.

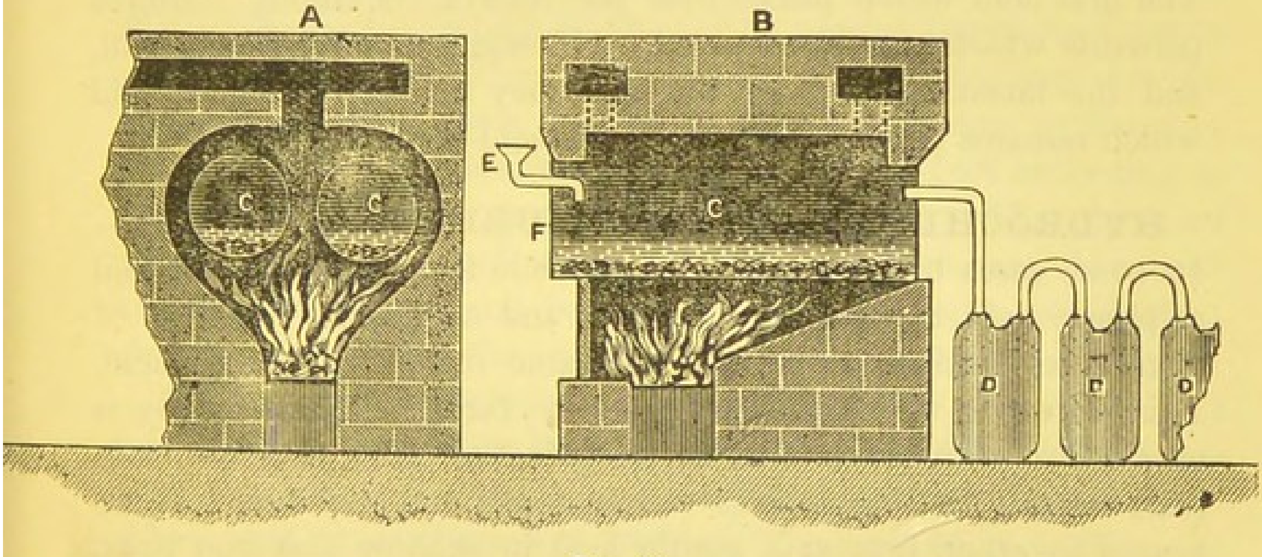

FIG. 11.

The reaction is carried out in large cylindrical retorts of cast iron, each about 2 ft. in diameter and 5 ft. long. These are set horizontally over a fire as shown in the accompanying figure, the flues being arranged so as to carry the fire gases completely round the retorts and keep the whole surface heated. The charge for such a retort would consist of 5 cwt. of the nitrate and 4 cwt. of sulphuric acid, the latter being always employed in excess of the proportion indicated by the equation

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

so that the residue left at the end of the operation may remain fluid enough to admit of its being readily run off. The front and back of the retort are closed by means of flagstone and occasionally the retort is lined in its upper part with acid-resisting brick, but unless the acid vapours are allowed to cool and condense they do not act upon the cast iron.

The condensation and collection of the acid is usually effected in a series of stoneware Woulff's bottles.

This process will yield acid of such a strength as to contain 60 per cent. HNO_3. If stronger acid is required concentrated sulphuric acid must be used and care taken to have the saltpetre dry. With these precautions, acid containing over 90 per cent. HNO_3 may be obtained, and by adding more sulphuric acid to this and redistilling, practically all the water may be removed. The first acid which passes over the retorts containing nitrogen peroxide which may be removed by blowing air through the acid, and the latest portions of the acid may contain sulphuric acid which remains behind when the crude acid is redistilled.

HYDROCHLORIC ACID OR MURIATIC ACID HCl.—In some cases hydrochloric acid is made from common salt and sulphuric acid in cylindrical retorts, and condensed in series of stoneware bottles quite after the same manner as nitric acid. This, however, is exceptional and by far the largest supply is obtained as a by-product in the manufacture of sodium sulphate (salt cake). In this process common salt and sulphuric acid are heated together, first at a gentle heat in shallow cast-iron pans. The gas which is given off during this process contains air, steam, and most of the hydrochloric acid, it is known as *pan-gas*

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

The residue is then raked out of the pans and heated in a reverbatory furnace to a much higher temperature, when a further quantity of hydrochloric acid is given off in the *roaster-gas*

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The point to which attention must be devoted here is the method employed for dealing with the heated mixture of air, steam and hydrochloric acid so that the last-named product may be condensed or absorbed as completely as possible. If the hydrochloric acid gas were not largely mixed with air and steam, and the temperature were low, the condensation would be easily effected by contact with water.

A charge of 16 cwt. of common salt with the requisite amount of sulphuric acid (sp. gr. 1·16) has been found to yield approximately

700 lbs. of HCl and 500 lbs. steam as "pan" gas.
and 360 „ „ 100 „ „ "roaster" gas.

The temperature of the pan gas will be at least 150° C., and that of the roaster gas not less than 500° C., and the cooling and condensation of such a product admixed with much air would require such large quantities of water that the acid obtained would be extremely weak.

It is essential therefore to dissipate some of the heat by a preliminary cooling which is effected by passing the gases through earthenware pipes before they reach the condensing towers. These earthenware pipes are usually about 12 inches in diameter and may extend to a length of from 100 to 300 feet according to the temperature or state of dilution of the gas. The pipes are inclined so that the acid which condenses in them may flow back towards the furnace and be intercepted at intervals in flagstone cisterns provided for the purpose.

The "condensers" proper are towers 50 feet or more high and 5 feet square, generally built of flagstone and filled with large coke, over which the water used for absorbing the residual hydrochloric acid gas is allowed to trickle. The acid which collects in the cisterns contains about 30 to 35 per cent. HCl, whilst that formed in the condensers does not exceed 28 per cent.

The strongest hydrochloric acid obtainable contains about 43 per cent. HCl and is prepared by passing the gas through water to saturation.

SULPHURIC ACID, OR OIL OF VITRIOL, H_2SO_4. We have seen that under certain circumstances sulphur dioxide combines with oxygen to form sulphur trioxide, and that this in presence of water gives sulphuric acid. The oxidation of sulphurous acid to sulphuric acid also takes place slowly when its aqueous solution is exposed to air at ordinary temperatures.

Such methods are, however, not suitable for the production of large quantities[1] of sulphuric acid as an article of commerce.

The oxidation of sulphurous acid is effectually performed by the intervention of the oxides of nitrogen, and on the large scale sulphur dioxide, oxygen (supplied in the form of air) and steam are brought together, and these in presence of oxides of nitrogen form sulphuric acid.

The *sulphur dioxide* in works where a very pure acid is made is obtained by burning brimstone, but in the very large majority of cases iron pyrites is used as the source of the gas. This is burnt in a series of "kilns," and the heat arising from the combustion is sufficient to render the operation continuous, fresh charges being added from time to time.

$$2\ Fe\ S_2 + 11\ O = Fe_2O_3 + 4\ SO_2.$$

The *nitric acid* from which the oxides of nitrogen are derived is prepared by the action of concentrated sulphuric acid on Chili saltpetre, $NaNO_3$—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3;$$

the acid fumes are carried into the flues along which the sulphur dioxide and air pass, and there intermingle with these gases.

The *air* is drawn in through the pyrites burners or kilns, the draught being maintained by means of a chimney, and by adjustment of the doors of the kilns so as to admit the quantity of air which experience has shown to be necessary.

The *steam* is supplied from low pressure boilers, and introduced into the "chambers" in such a way as to become intimately associated with the other products.

The reaction ending in the production of sulphuric acid does not take place under the circumstances very rapidly, and it is necessary to provide for a lengthened period of contact between

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[1] Over a million tons of oil of vitriol are produced in Great Britain alone in the course of a year.

the various bodies which take part in it. The gases are led into a series of large chambers where they meet with the steam. These are usually three in number, and have a total capacity of 100,000 to 150,000 cubic feet, the relation of the sulphur burnt to the capacity of the chamber being such that the average time occupied by the gas in traversing the chambers is something like three hours. The walls and floor of the chambers are constructed of sheet-lead supported on a wooden framework, lead being a metal which is scarcely attacked at all by sulphuric acid of the strength produced in the chambers. The chambers are kept cool enough to serve as condensers, so that the acid collects on the floor, and is drawn off periodically.

The recovery of the oxides of nitrogen.—In practice, the higher oxides of nitrogen are carried forward in the chambers, and would escape at the exit. To avoid this waste, advantage is taken of the fact that they are absorbed by *concentrated* sulphuric acid. The exit gases from the chambers are therefore passed through a tower (known as the *Gay-Lussac tower*), packed with coke, down which concentrated sulphuric acid constantly trickles. The oxides of nitrogen taken up in this way are discharged again if the acid be diluted, since they are practically insoluble in *dilute* sulphuric acid.

In order therefore to render these absorbed gases again available in the production of sulphuric acid, the acid which has traversed the Gay-Lussac tower is pumped up to the top of a *Glover tower* placed at the entrance of the chambers. This tower is packed with flints and coke, and the nitrated acid is diluted as it runs down by being mixed with the weaker "chamber acid." The oxides of nitrogen which have been absorbed in the Gay-Lussac tower are thus discharged within the Glover tower, and there mix with the gases which are passing from the pyrites burners to the chambers, the Glover tower being placed between the pyrites burners and the chambers. The Glover tower performs the further function of cooling the gases before they enter the chambers, and in addition to this, a considerable amount of sulphuric acid is actually formed in the Glover tower itself. The acid which escapes from the Glover is strong (80 per cent.), and has a temperature of 120° to 130°.

PLANT FOR MANUFACTURE OF SULPHURIC ACID. SCALE 18 FT. TO THE INCH.

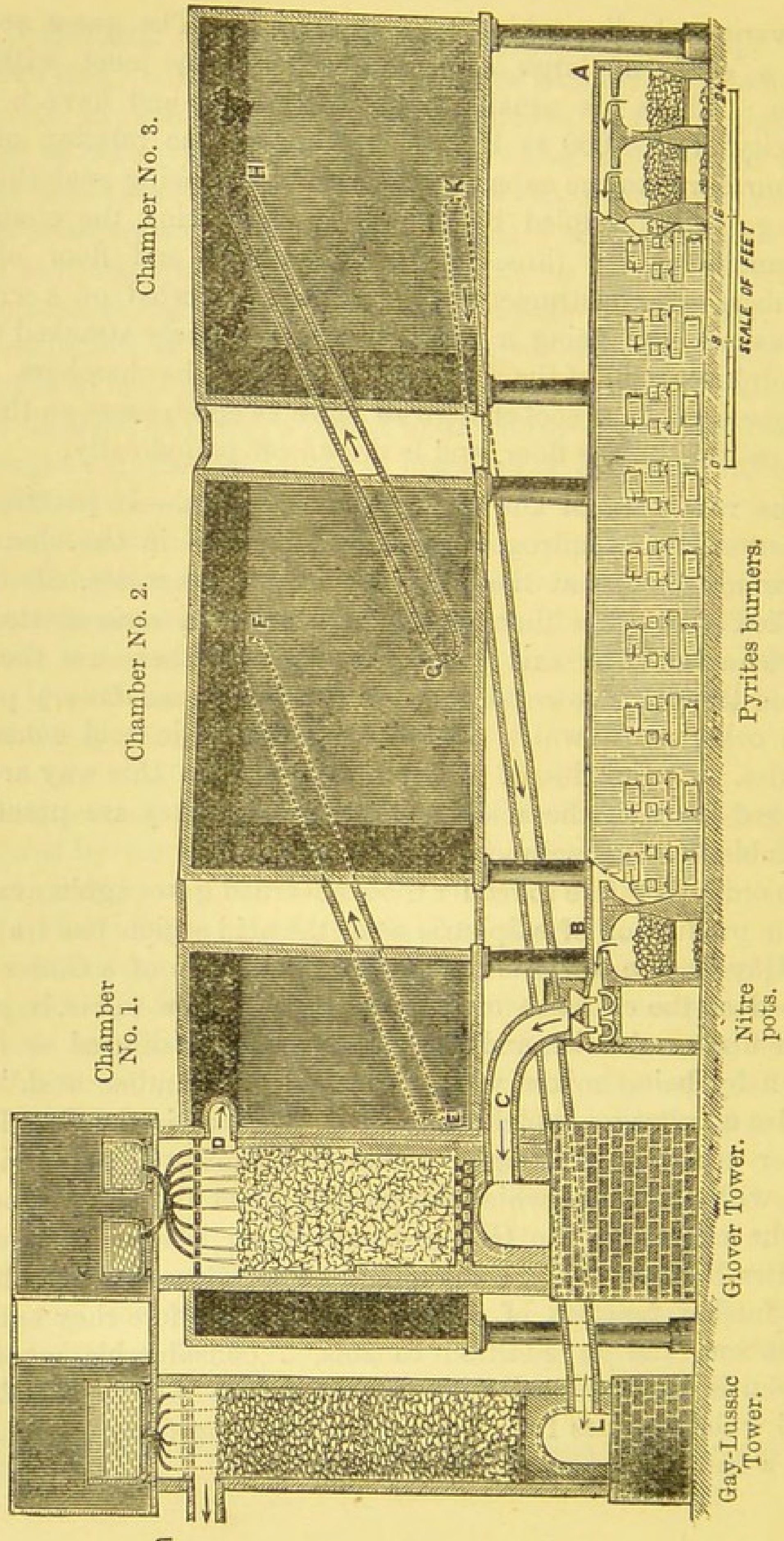

Fig. 12.

Details relating to Sulphuric Acid plant. Fig. 12.

(1) **Pyrites burners.**—These are shown partly in section, so as to indicate the charge and the common flue into which the gas passes. There are 24 burners, a second row of 12 being placed back to back with those shown. The various doors on the front of the burners serve for charging the ore, stirring the charge when necessary, and finally for removing the burnt ore which has fallen into the ashpit underneath.

(2) **The Glover tower.**—This is packed with flints, through which trickle from the tanks above (*a*) strong nitrated acid, which has been previously used to absorb nitrous fumes in the Gay-Lussac tower (*b*), weak chamber acid. When the two acids mix, nitrous fumes are freely liberated within the tower, and thus it supplements the nitre-pots in providing the nitrous fumes necessary for the process.

(3) **The Gay-Lussac tower.**—This is packed with coke, and the strong acid (sp. gr. 1·78) which is supplied from the tank above, passes over the coke and absorbs any nitrous fumes in the exit gases from the chambers.

The course taken by the gases.—The sulphur dioxide and air (in excess) pass along the common flue A B from the pyrites burners over the nitre-pots, and then along the pipe C, through the Glover tower. At D they pass in at the front of chamber No. 1, and thence from the back at E to the back of chamber No. 2, entering this at F by the pipe E F. Similarly by G H from the front of chamber No. 2 to the front of No. 3, and from the back of this to the base of the Gay-Lussac tower by K L. Having traversed the Gay-Lussac tower the exit gas finally passes off to the chimney by the outlet at the upper part of the tower. The steam is blown in at the ends of the chambers in such a way as to travel always in the direction of the draught, that is to follow the same course as that taken by the gases. Each chamber is 25 ft. wide, 20 ft. high, and 100 ft. long, and they are seen in the figure in transverse section, so that the direction of the length would be perpendicular to the plane of the paper.

The functions of the various parts of the sulphuric acid plant may be summed up thus—

The Chambers (1) bring about a prolonged contact between the reacting bodies.

(2) Condense the sulphuric acid which collects as the chamber acid (sp. gr. 1·6, containing nearly 70 per cent. H_2SO_4) on the floor of the chamber.

The Gay-Lussac Tower absorbs the oxides of nitrogen in the *exit* gases from the chamber.

The Glover Tower (1) effects discharge of oxides of nitrogen from the nitrated acid produced in Gay-Lussac tower.

(2) Cools the gases from the pyrites burners, the heat so absorbed concentrating the acid to sp. gr. 1·75, or 80 per cent.

(3) Assists in the actual production of sulphuric acid.

At a higher degree of concentration sulphuric acid rapidly attacks lead, and if stronger acid is needed, the concentration is effected by boiling it in glass or platinum stills, when *very weak* acid passes over, and the acid remaining in the still rises in strength till it contains 95 to 98 per cent. H_2SO_4.

Acid containing 100 per cent. H_2SO_4 cannot be obtained by distillation alone. It is prepared by adding sulphur trioxide to the 98 per cent. acid, and then on freezing, crystals of pure H_2SO_4, melting at 10° C., separate out.

Properties of sulphuric acid.—The pure concentrated acid is a thick oily liquid (sp. gr. 1·84), from whence it derives the name, *oil* of vitriol. It boils at 338° C., with partial decomposition, so that when the acid containing 100 per cent. H_2SO_4 is distilled the residue becomes weaker, until it reaches a strength of about 96 per cent. H_2SO_4, at which it remains constant.

It is highly corrosive, charring wood and many organic substances even at the ordinary temperature. This is largely owing to the great avidity with which it takes up water. Wood consists mainly of cellulose, a compound of carbon, and hydrogen and oxygen in the proportions in which they are contained in water: the acid therefore abstracts water, leaving a mass of carbon. The concentrated acid is frequently used for drying the ordinary gases. Its affinity for water is likewise shown by the large amount of heat evolved when the two liquids are mixed.

Laboratory representation of the Sulphuric Acid Manufacture.

The formation of sulphuric acid may be represented in the laboratory by taking a large flask (5 litres) and fitting it with a cork provided with five holes through which pass tubes delivering—

(1) Sulphur dioxide
(2) Nitric oxide
(3) Steam,
(4) Oxygen from a gasholder;

while the fifth hole is provided with a tube opening into the air. The arrangement is shown in the figure.

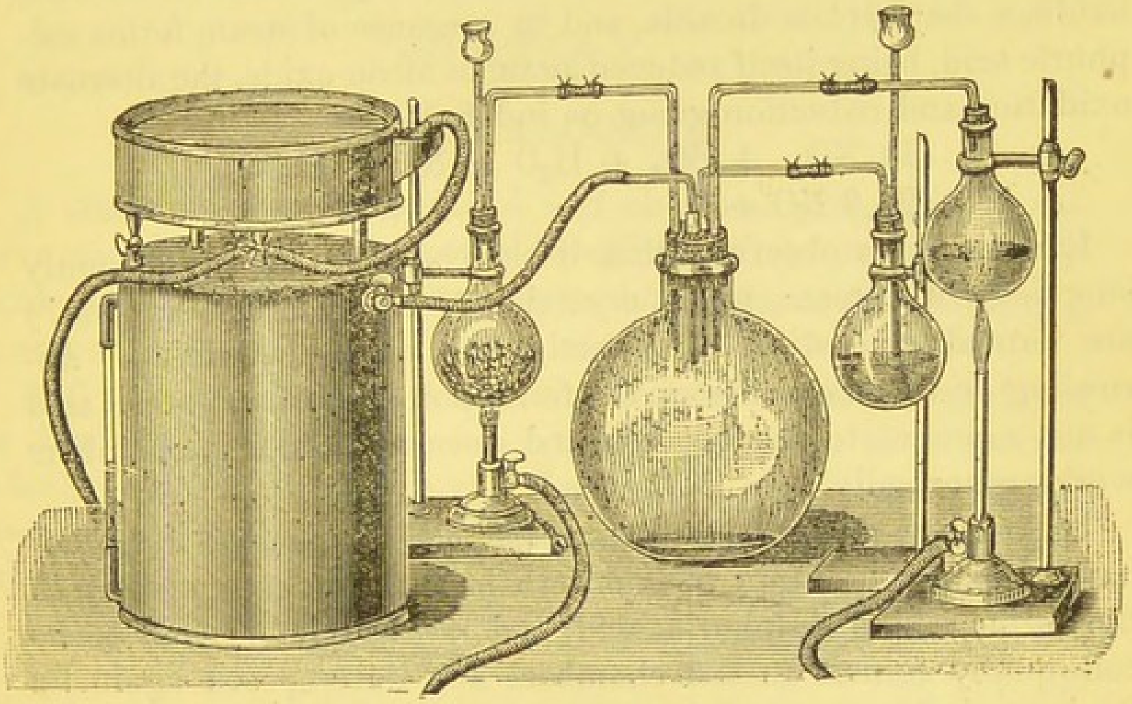

FIG. 12A.

Pass some sulphur dioxide, nitric oxide, steam, and oxygen into the flask, then shut off the steam supply; crystals of nitrosulphonic acid (lead chamber crystals) may be seen to form. On clearing the flask of red fumes by a current of oxygen, and then passing in more steam, these crystals will dissolve with the evolution of red fumes. After allowing the reaction to go on for some minutes, the liquid condensed in the flask may be tested for sulphuric acid

The theory of the Sulphuric Acid Manufacture.--By the action of the oxygen in air and moisture, in the form of steam, sulphur dioxide is transformed into sulphuric acid, but the change takes place very slowly, and the sulphuric acid obtained is extremely dilute. In presence of certain substances, notably the higher oxides of nitrogen as in the sulphuric acid chambers, the conversion is more rapid: but much difference of opinion exists as to the actual changes which take place, and even as to the particular oxides of nitrogen which take part in the reaction.

The older theory, originally suggested by Berzelius, regards the nitric oxide (NO) as the body which brings about the formation of the sulphuric acid. This it does by taking up oxygen from the air and forming nitrogen peroxide (NO_2), which in its turn oxidizes the sulphur dioxide, and in presence of steam forms sulphuric acid, being itself reduced again to nitric oxide, the alternate oxidation and reduction going on indefinitely:—

$$(1)\ NO_2 + SO_2 + H_2O = NO + H_2SO_4.$$
$$(2)\ 2\,NO + O_2 = 2\,NO_2$$

It is however observed that if the chambers are insufficiently supplied with steam, white crystals ("lead chamber crystals") are formed, consisting of nitrosulphonic acid, SO_2OHNO_2. According to the above theory the formation of nitrosulphonic acid is not essential to the process, and does not occur in chambers working normally.

The theory more recently proposed by Lunge on the other hand assumes nitrogen trioxide[*] to be the true intermediary in the formation of sulphuric acid, and nitrosulphonic acid to be continually formed in the chambers and decomposed again by the excess of steam according to the equations—

$$(3)\ 2\,HNO_3 + 2\,SO_2 + H_2O = 2\,H_2SO_4 + N_2O_3.$$
$$(4)\ N_2O_3 + O_2 + 2\,SO_2 + H_2O = 2\,SO_2OHNO_2.$$
$$(5)\ 2\,SO_2OHNO_2 + H_2O = N_2O_3 + 2\,H_2SO_4.$$

Under some conditions, and especially where the gases are just entering the chambers and sulphur dioxide is in large excess, it is however admitted that nitric oxide plays a prominent part. With this exception Lunge's theory is not inconsistent with the observations recorded in actual working on the large scale.

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[*] The theory holds if N_2O_3 be regarded as a mixture of NO_2 and NO

CHAPTER V.

THE HALOGENS.

A COMPARISON of the physical and chemical properties of the four elements, fluorine, chlorine, bromine, and iodine, and of their compounds, readily lead one to regard these elements as forming a natural group.

And this not so much from the closeness of the resemblance as from the fact that there is a gradual transition in properties which proceeds always in the same order, viz. in the order of their atomic weights. A general survey of the group will illustrate this.

Physical properties of these elements.—Fluorine is a gas which condenses to a liquid when cooled down to — 187° C. ; the gas possesses a very faint greenish-yellow colour ; chlorine is condensed to a liquid at — 34° C, the gas has a distinct greenish colour ; bromine is a reddish-brown liquid boiling at 59° C. and solidifying at — 7° C., whilst iodine is a black crystalline solid which boils at 184° C., its vapour being of a beautiful violet colour.

In the gaseous condition these elements have a very irritant action on the mucous membrane which is most marked in the case of fluorine and chlorine, and least so with iodine. They have an odour resembling that of seaweed if they are in a largely diluted condition.

Their solubility in water follows the order of their atomic weight; chlorine, the most soluble (fluorine decomposes water), dissolving in about half its volume of water, bromine to the extent of three parts in 100 of water, whilst iodine is only very slightly soluble in water, but dissolves readily in alcohol, ether, bisulphide of carbon, or in a solution of potassium iodide.

When chlorine is passed into water to saturation at 0° C., yellow crystals having the composition $Cl_2 . 8 H_2O$ separate out. On warming these crystals they readily decompose with the evolution of chlorine. Bromine under similar circumstances forms crystals having the composition $Br_2 . 10 H_2O$.

General Chemical Properties.—Whilst the tendency to combine with oxygen *increases* as we pass from fluorine to iodine, the affinity for hydrogen and the metals *decreases*. Fluorine forms no compound with oxygen, chlorine can only be made to combine indirectly and forms unstable oxides, iodine however is directly oxidized by nitric acid, and its oxide is much more stable. Hydrogen, on the other hand, combines directly even *in the dark* with fluorine and at very low temperatures, but with chlorine the combination only takes place on heating or under the stimulus of rays of light of great chemical activity, and bromine and iodine are induced to combine with hydrogen with much greater difficulty.

Moreover, the stability of the products of such action, HF, HCl, HBr, HI, shows a falling off in the order named.

The interaction of the halogens and water is instructive. Fluorine decomposes water immediately at ordinary temperatures, and with considerable energy, giving rise to the formation of ozone. Chlorine acts at ordinary temperatures only in presence of sunlight, and bromine and iodine are without action.

Fluorine.—The isolation of a substance which even at ordinary temperatures decomposes water and other compounds, and attacks solid substances with great readiness, cannot but be attended with difficulty, and it was not till 1887 that fluorine was obtained in the free state. Moissan accomplished this by the electrolysis of liquid hydrofluoric acid perfectly free from moisture. Liquid hydrofluoric acid is however a non-conductor of electricity, and it was necessary to add to it potassium hydrogen fluoride

(KHF_2) to enable it to conduct the current. The apparatus used in the decomposition consists of a platinum U tube. This tube, which is shown in the figure, is provided with side tubes to lead off the hydrogen which is evolved at the negative pole, and the fluorine from the positive pole.

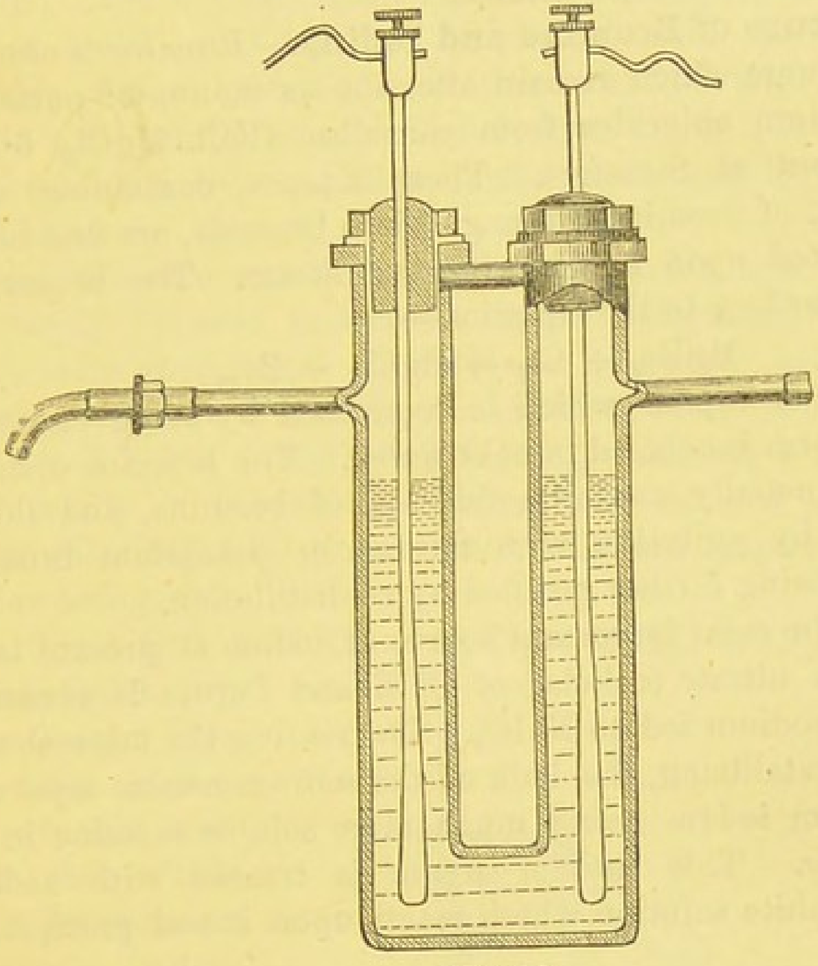


FIG. 13.

The negative pole consists of platinum, and the positive pole of an alloy of platinum and iridium, which is less rapidly acted upon by fluorine than any other metal, and these are fitted into the U tube by means of fluor-spar stoppers, which close the end of the U tube gas-tight. Liquid hydrofluoric acid, being a very volatile substance at ordinary temperatures, the apparatus is kept at – 23° C.

Fluorine acts with great energy on mercury, sodium, potassium, and magnesium, etc., and less violently on such metals as copper, silver, platinum. Bromine, iodine, carbon, sulphur, silicon, phosphorus, and arsenic likewise combine immediately with the production of flame at ordinary temperatures, fluorides of these elements being formed. Not only water, but the haloid acids, also sulphur dioxide, sulphuretted hydrogen, ammonia, and even silica, are decomposed at once. In fluorine we have then the most active chemical substance known.

Manufacture of Bromine and Iodine.—*Bromine* is obtained from the liquors which remain after the extraction of potassium and magnesium chlorides from carnallite ($KCl.\ MgCl_2.\ 6\ H_2O$) as carried out at Stassfurt. These liquors, containing about 0·25 per cent. of bromine, as magnesium bromide, are first heated and then acted upon by chlorine and steam. The bromine is liberated according to the equation—

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2,$$

and escapes as vapour which is condensed by being caused to traverse a worm immersed in cold water. The bromine obtained in this way usually contains chloride of bromine, and this is decomposed by agitation with ferrous or potassium bromide, the bromide being further purified by re-distillation.

Iodine.—The most important source of iodine at present is the crude sodium nitrate (caliche) of Chili and Peru. It occurs in this body as sodium iodate $NaIO_3$. On treating the mineral with water and crystallizing, the bulk of the sodium nitrate separates, and the sodium iodate being much more soluble remains in the mother liquor. This mother liquor is treated with sodium hydrogen sulphite solution which reacts upon it and precipitates the iodine—

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

The iodine is allowed to settle out, and then washed and pressed into cakes, being finally resublimed at as low a temperature as possible.

In Scotland, iodine is extracted from deep-sea weed, which contains from about 0·27 to 0·47 per cent. of iodine. The best process in use for obtaining this iodine is the following—

The weed, which must after collecting be kept dry until used, is boiled with sodium carbonate and filtered: the filtrate is treated with hydrochloric acid and again filtered, the filtrate in this case being neutralized with caustic soda, evaporated to dryness, and carbonized. The two filtrations have separated two organic bodies resembling cellulose and albumen respectively, and which have found several useful applications. The carbonized residue is treated with warm water, and evaporated until all the less soluble salts (chiefly potassium sulphate and chloride) have crystallized out. The mother liquor is treated with a small quantity of sulphuric acid to decompose sulphides and sulphites. It is then distilled with manganese dioxide and sulphuric acid, the former being added in small quantities at a time. Iodine distils over and is purified by resubliming.

In the laboratory, sodium chloride, bromide and iodide may respectively be used as sources of the halogens. These when treated with manganese dioxide and sulphuric acid give the following reaction, R standing for chlorine, bromine or iodine—

$$2\,NaR + 3\,H_2SO_4 + MnO_2 = 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + R_2.$$

More usually in preparing chlorine, concentrated hydrochloric acid is substituted for the common salt and sulphuric acid, the reaction being—

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

The reaction may be performed in a flask fitted with a safety funnel similar to that which would be used in preparing hydrochloric acid; very gentle heat is required. In the preparation of bromine and iodine a small glass retort such as is shown in the accompanying figure is more convenient, the bromine and iodine condensing either in the neck of the retort or in a small receiver which is kept cool by means of a stream of water.

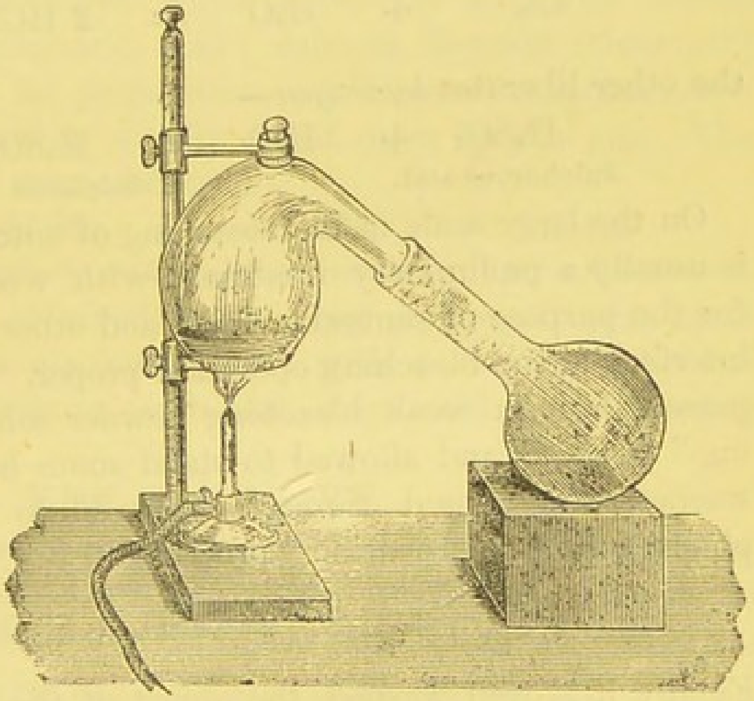


FIG. 14.

The bleaching of vegetable coloring matters.—Chlorine and to a slight extent bromine possesses the property of depriving the leaves of plants, flowers and vegetable dyes of their colour. In the absence of moisture no such action however takes place, the bleaching being due to the oxidation of the colouring matter by *nascent* oxygen resulting from the interaction of chlorine and water. Certain oxidizing agents which likewise furnish nascent oxygen, notably hydrogen peroxide, have a similar action.

If a piece of cloth dyed with turkey-red be placed in a stoppered jar of dry chlorine, and left for some minutes no decolourization will occur, but if the cloth is moist it will be bleached.

As *oxidizing agents* are those which really transfer oxygen to other substances which are thereby subjected to oxidation, so *reducing agents* are those which take away oxygen and effect reduction. Sulphur dioxide is a typical reducing agent; its powers as an antiseptic and as a medium for bleaching silk, &c., being due to its affinity for oxygen. Chlorine bleaches in consequence of its bringing about the oxidation of the colouring matter; sulphur dioxide bleaches, on the contrary, in consequence of its reducing action. The one liberates *oxygen* from water—

$$Cl_2 + H_2O = 2\,HCl + \underset{\text{Nascent oxygen.}}{O}$$

the other liberates *hydrogen*—

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4} + H_2$$

On the large scale in the bleaching of cotton cloth or linen there is usually a preliminary treatment with weak solutions of alkali for the purpose of removing fatty and other matters which would interfere in the bleaching operation proper. The material is then passed through weak bleaching powder solution (the "chemicking" process) and allowed to stand some hours, after which it is washed and passed through very dilute hydrochloric or sulphuric acid (the "souring" process)

$$Ca{<}^{Cl}_{OCl} + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

Finally it is well washed, the object of the souring and washing being to decompose and remove any bleaching agent which still remains and the oxidized colouring or other matters.

Compounds of Hydrogen with the Halogens.—The chemical affinity of these elements for hydrogen and for metals shows a gradation from fluorine to iodine *decreasing with the increase of atomic weight.* Thus, if we consider the stability of the compounds of these elements with hydrogen, we find that whilst hydrofluoric acid may be strongly heated without decomposition, hydriodic acid is decomposed almost completely by exposure to light, or by heating to dull redness.

Also, fluorine combines with hydrogen directly under all circumstances, and will, as we have seen, even decompose water at ordinary temperatures by reason of its great affinity for hydrogen. Chlorine, however, only combines with hydrogen under the stimulus of heat or light, and the direct combination with bromine and iodine is effected with difficulty.

It is worthy of remark that their affinity for oxygen, on the contrary, *increases* with the increase of atomic weight, so that fluorine has not under any circumstances been induced to combine with oxygen; it is indeed *the only element* which forms no compound with oxygen.

Preparation and Properties of Hydrofluoric Acid, HF.—This gas is obtained when a fluoride is gently heated with concentrated sulphuric acid; calcium fluoride (fluorspar) is generally used in its preparation, a platinum or leaden retort being used, since glass is rapidly acted upon by the gas. The equation representing the reaction is—

$$\underset{\text{Calcium fluoride.}}{CaF_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Calcium sulphate.}}{CaSO_4} + \underset{\text{Hydrofluoric acid.}}{2\,HF}$$

The pure acid is obtained by heating hydrogen potassium fluoride, KHF_2, in a platinum retort with a delivery tube and receiver both of platinum and both kept cool by a freezing mixture:—

$$KHF_2 = HF + KF$$

Hydrofluoric acid at ordinary temperatures is a highly corrosive gas, which fumes in moist air, and may be condensed to the liquid form in a freezing mixture; this liquid boils at 19° C. The gas at ordinary temperatures has a density of 20, corresponding to the formula H_2F_2, but on gently warming, its density diminishes rapidly, and approaches the value 10, corresponding to the formula HF. It is readily soluble in water, giving an *acid reaction*, and the aqueous solution may conveniently be used for demonstrating its properties.

An examination of the elementary properties of the gas may be made without actually collecting the gas. The powdered fluorspar is *gently* warmed in a small leaden dish, with so much sulphuric acid as will make it into a thin paste. The fumes of the gas must not be inhaled, nor should the acid in any form be allowed to come in contact with the fingers.

Coat a watch-glass with a thin layer of bees-wax, scratch on it some device, and expose to the fumes rising from the dish. The surface of the glass, where the wax has been removed, will be acted upon, the silica of the glass being converted into the volatile silicon tetrafluoride, thus—

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

Hydrofluoric acid attacks most metals and oxides with the formation of fluorides. The acid fluorides of the alkali metals like hydrogen potassium fluoride (KHF_2) should be noticed, because the other halogen acids do not form such salts. It may be remarked also, that when hydrogen fluoride is quite free from water it does not attack glass: similarly perfectly dry hydrogen chloride does not attack sodium.

The preparation of Hydrochloric Acid Gas, HCl.—As the student will already be familiar with the preparation of this gas it is not necessary to give it here.

The preparation of Hydrobromic and Hydriodic acids. These compounds are best prepared by the action of water upon the phosphorus compounds of bromine and iodine.

Phosphorus combines directly with bromine and iodine, forming PBr_5 and PI_5 respectively. These compounds are immediately acted upon by water thus—

$$\underset{\text{Phosphorus penta-bromide.}}{PBr_5} + 4\ H_2O = \underset{\text{Phosphoric acid.}}{H_3PO_4} + \underset{\text{Hydrobromic acid.}}{5\ HBr.}$$

$$PI_5 + 4\ H_2O = H_3PO_4 + \underset{\text{Hydriodic acid.}}{5\ HI.}$$

It is not necessary to previously prepare the penta-bromide or penta-iodide of phosphorus, for if amorphous phosphorus and water are introduced into a flask, and bromine or iodine are added *very gradually*, and then the flask is gently warmed, the hydrobromic or hydriodic acid gas is given off.

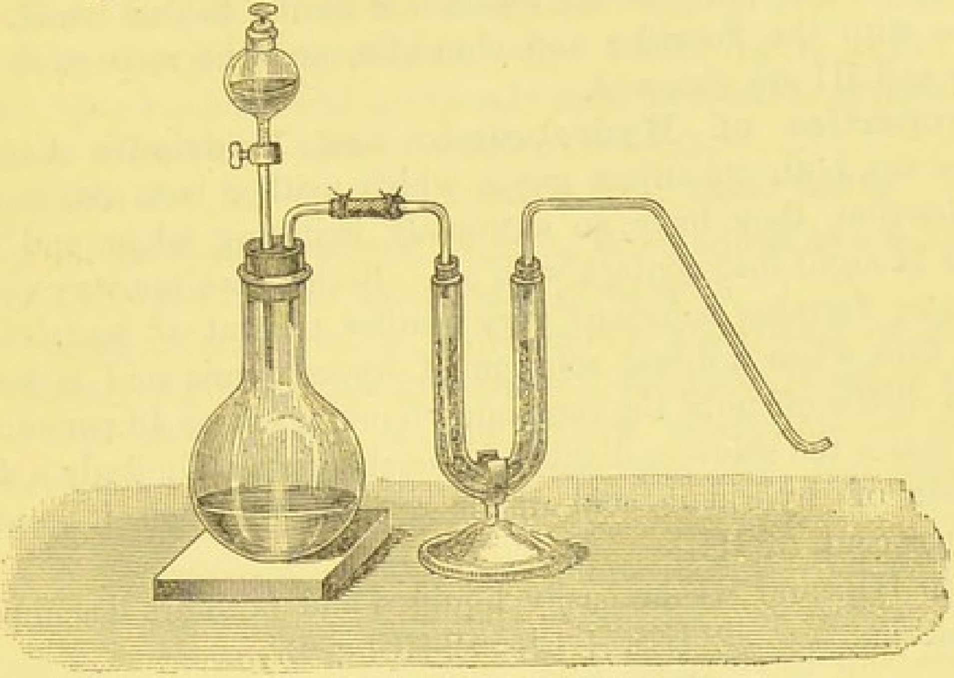


FIG. 15.

It is first passed through a U tube, as shown in Fig. 15, containing amorphous phosphorus, to absorb any free bromine or iodine that may be carried over, and then collected by downward displacement or over mercury. Both these gases dissolve very readily in water, and form strongly acid solutions.

Bromides and iodides, like fluorides and chlorides, might be expected to undergo decomposition when treated with concentrated sulphuric acid, evolving hydrobromic and hydriodic acids respectively; but as a matter of fact these acids are so unstable that they themselves decompose in presence of sulphuric acid. Free bromine and iodine are therefore obtained in this reaction, whilst the hydrogen which is liberated in the solution acts upon the sulphuric acid, reducing it to sulphurous acid—

$$(1)\ 2\,H_2SO_4 + 2\,KI = 2\,KHSO_4 + 2\,H + I_2.$$

$$(2)\ H_2SO_4 + 2\,H = H_2SO_3 + H_2O.$$

Summing these two reactions together, we have—

$$(3)\ 3\,H_2SO_4 + 2\,KI = 2\,KHSO_4 + H_2SO_3 + H_2O + I_2.$$

The H_2SO_3 is too unstable to exist as such, and breaks up into $H_2O + SO_2$, so that in reality we obtain

$$2\,KHSO_4 + SO_2 + 2\,H_2O + I_2$$

as the final product. By using, instead of sulphuric acid, an acid such as phosphoric acid, which does not so readily undergo reduction, the course of the reaction is similar to that which takes place with the fluorides and chlorides, and the respective acids HBr and HI are obtained.

Properties of Hydrobromic and Hydriodic Acids.—These are both colourless gases, which neither burn nor support combustion, they have an extremely irritating odour and fume when brought into contact with air. Both gases are very soluble in water forming solutions very similar to that of hydrochloric acid, thus when a dilute solution of hydrobromic acid is heated, water distils off until the remaining liquid contains 48 per cent. of HBr when the solution distils over unchanged. Similarly a dilute solution of hydriodic acid distils unchanged when it contains 57·7 per cent. of HI.

Both HBr and HI are easily liquified and both are decomposed by chlorine $2\,HBr + Cl_2 = 2\,HCl + Br_2$

$$2\,HI + Cl_2 = 2\,HCl + I_2$$

The Salts of the Haloid Acids.—By the replacement of the hydrogen in the haloid acids by metals, fluorides, chlorides, bromides and iodides are formed;

$$KHO + HI = KI + H_2O$$

these form a distinct class of salts, differing from all others in containing no oxygen. The methods of preparing these haloids salts are :—

(1) Direct combination of elements with the halogens.

(2) Solution of the metal, the oxide, hydrate, or carbonate in the acid.

(3) The addition of the acid or a soluble haloid salt to a solution of a salt of the metal with the production of an insoluble, or slightly soluble, haloid salt.

The chlorides, bromides and iodides resemble one another very closely, being soluble in water with very few exceptions, *i.e.* the mercurous, silver and lead salts. The alkaline bromides are decomposed by chlorine and alkaline iodides by both chlorine and bromine, thus when chlorine water is added to a solution of KBr, the liquid becomes brown from the liberation of bromine.

$$2\,KBr + Cl_2 = 2\,KCl + Br_2.$$

By shaking the liquid with a few drops of chloroform the bromine dissolves out, forming a deep red solution.

The fluorides differ from the other haloid salts in many respects thus silver fluoride is soluble in water whilst AgCl, AgBr, and AgI are each insoluble and conversely calcium fluoride is insoluble whilst the other haloid salts of calcium are soluble.

Tests for the halogen acids and their salts.

1. A solution of silver nitrate, $AgNO_3$, when added to a solution of a halogen acid or haloid salt, gives with

   Hydrochloric acid, a white curdy precipitate of silver chloride AgCl, soluble in ammonia, insoluble in nitric acid.

   Hydrobromic acid, a pale yellow precipitate of silver bromide, AgBr, soluble in strong ammonia, insoluble in nitric acid.

   Hydriodic acid, a yellow precipitate of silver iodide, AgI, insoluble in ammonia and nitric acid.
2. Free HCl, HBr, or HI, heated with manganese dioxide, or their salts, heated with manganese dioxide and sulphuric acid, evolve chlorine, bromine, and iodine respectively, and these elements are easily recognized by their colour, smell, and bleaching action.
3. Chlorine water (which must not be in excess) added to a bromide or iodide liberates bromine or iodine, and on shaking the liquid with carbon bisulphide, the bromine imparts to it a red colour and the iodine a violet colour.

Oxides and Oxy-Acids of Chlorine.—Only two oxides of chlorine (Cl_2O and ClO_2) are known, and these are very unstable bodies, and readily undergo decomposition with explosion.

Chlorine monoxide, Cl_2O, is prepared by the action of *dry* chlorine on well-cooled and freshly precipitated mercuric oxide.

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

Chlorine peroxide, ClO_2, is obtained by the action of sulphuric acid on potassium chlorate. The sulphuric acid, of which a large excess is taken, must be kept cool in a freezing mixture and the potassium chlorate added little by little; on gently heating, ClO_2 is given off as a yellow gas. *Euchlorine*, which is obtained on warming potassium chlorate with concentrated hydrochloric acid, consists of a mixture of this gas with chlorine.

Three oxy-acids of chlorine are known—

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

Hypochlorous acid, $HClO$, is a very unstable body, and only known in dilute solution. The free acid is a powerful bleaching agent. Hypochlorous acid may be prepared—

(1) By shaking up together precipitated mercuric oxide and chlorine water. We have seen that in the *absence* of water Cl_2O is formed.

(2) By distilling a solution of a hypochlorite with *very dilute* nitric acid.

Hypochlorites may be prepared by the action of chlorine on caustic alkalies when *kept quite cool*—

$$2\,NaOH + Cl_2 = NaCl + \underset{\text{Sodium hypochlorite.}}{NaClO} + H_2O$$

The most important derivative of this acid is bleaching powder, obtained by passing chlorine over dry calcium hydrate. Mineral acids or even carbon dioxide act on the hypochlorites and liberate chlorine, and it is for use in this way that bleaching powder is produced on a large scale.

Chloric acid, $HClO_3$.—The acid has not been obtained anhydrous, the strongest chloric acid containing more than half its weight of water. In this form it is a syrupy liquid which readily decomposes by heat or in presence of oxidizable substances. It is obtained by adding dilute sulphuric acid to a solution of barium chlorate in just sufficient quantity to combine with the whole of the barium.

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

The *chlorates* are all soluble in water. The alkaline chlorates are prepared by the action of chlorine on *hot concentrated* solutions of caustic alkalies, the reaction taking the form—

$$6\,KOH + 3\,Cl_2 = \underset{\text{Potassium chlorate.}}{KClO_3} + 5\,KCl + 3\,H_2O.$$

The chlorate being much more insoluble, can be readily separated from the chloride by crystallization.

Perchloric Acid, $HClO_4$.—Prepared by distilling potassium perchlorate in a small retort with concentrated sulphuric acid.

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4.$$

It is a heavy oily liquid which fumes in air, and although possessed of considerable stability in the pure condition, it readily decomposes in the presence of organic matter. It is a very powerful oxidizing agent, and detonates strongly when dropped on to dry charcoal; it sets fire to paper when brought into contact with it.

The perchlorates are soluble in water and are more stable than the chlorates. They are distinguished from the chlorates by yielding no euchlorine when warmed with hydrochloric acid.

When potassium chlorate is fused and the heat continued till the mass becomes pasty, potassium perchlorate is formed, the change which has taken place being—

$$2\ KClO_3 = KClO_4 + KCl + O_2.$$

The perchlorate, being more insoluble than the chloride, may be obtained by dissolving the mass in water and allowing the perchlorate to crystallize out.

If the chlorate be *strongly* heated for some time the whole of the oxygen is given off and the chloride remains as a residue—

$$2\ KClO_3 = 2\ KCl + 3\ O_2.$$

Oxy-acids of bromine.—No oxides of bromine are known, and of the oxy-acids only the *hypobromous acid*, $HBrO$, and the *bromic acid*, $HBrO_3$, have been prepared.

These are prepared by methods resembling those used for the corresponding chlorine compounds, with which they also agree in their general properties.

Oxides and oxy-acids of iodine.—Only one oxide of iodine, the *pentoxide*, I_2O_5, is known with certainty, whilst of the oxy-acids, *iodic acid*, HIO_3, and *periodic acid*, HIO_4, have been obtained.

Iodine pentoxide is a white crystalline powder obtained by heating iodic acid to 180° C.—

$$2\ HIO_3 = I_2O_5 + H_2O.$$

At 300° C. it is decomposed into iodine and oxygen.

Iodic acid.—Concentrated nitric acid has no action on chlorine, but when heated with iodine, iodic acid is formed. It is also produced when chlorine is passed into water in which iodine is suspended—

$$5\ Cl_2 + 6\ H_2O + 2\ I = 2\ HIO_3 + 10\ HCl.$$

It is soluble in water, and is a powerful oxidizing agent.

The **iodates**, like the chlorates, readily part with oxygen on heating, leaving iodides. They are formed by the action of caustic alkalies on iodine, the reaction either in the hot or cold solution taking a similar course to that which occurs with chlorine in the hot solution—

$$6\ KOH + 3\ I_2 = KIO_3 + 5\ KI + 3\ H_2O.$$

Periodic acid, HIO_4.—If perchloric acid be acted upon by iodine, periodic acid is formed and chlorine liberated—

$$2\ HClO_4 + I_2 = 2\ HIO_4 + Cl_2.$$

Periodates of the alkalies may be prepared by the action of chlorine on the iodate, and in presence of caustic alkali other periodates by double decomposition of these with soluble salts of the metals.

$$KIO_3 + 3\ KOH + Cl_2 = K_2H_3IO_6 + 2\ KCl.$$

Barium periodate is a body of great stability, and may be obtained by heating barium iodate to redness.

CHAPTER VI.

PHOSPHORUS.

Occurrence.—Phosphate of lime, $Ca_3(PO_4)_2$, the principal source of phosphorus, forms the essential constituent of the mineral apatite, and of bone-ash. The former occurs in the older formations of the earth's crust as—

$$\text{Chlorapatite, } 3\ Ca_3(PO_4)_2 \cdot CaCl_2;$$

$$\text{and Fluorapatite, } 3\ Ca_3(PO_4)_2 \cdot CaF_2.$$

Bone-ash is obtained by the dry distillation of bones.

In small quantities phosphates are very widely distributed, all fertile soils contain a small percentage, and they are always found in plants, being, like nitrogen, essential to plant-life.

Preparation of phosphorus.—The first step in the preparation of phosphorus from bone-ash consists in treating it with sulphuric acid, whereby a double decomposition takes place—

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 = 3\ CaSO_4 + 2\ H_3PO_4.$$

When the decomposition is complete, the product is filtered through a bed of cinders; the calcium sulphate remains on the filter, and the phosphoric acid passes through.

The liquid is then concentrated, mixed with charcoal, and further heated almost to dryness, the phosphoric acid losing water and being converted into metaphosphoric acid—

$$H_3PO_4 = HPO_3 + H_2O.$$

Finally, the granular product is heated to full redness in clay retorts placed horizontally in series over a fire, when the following reaction takes place—

$$2\ HPO_3 + 6\ C = H_2 + 6\ CO + 2\ P.$$

Luted into the mouth of each retort is an iron pipe, bent at right angles and dipping into water; the vapour of phosphorus is thus led into the water, and there condensed out of contact with air. The temperature of the water is high enough to keep the phosphorus in the liquid state, and it can be run off or ladled out from time to time. It is further refined by re-melting in

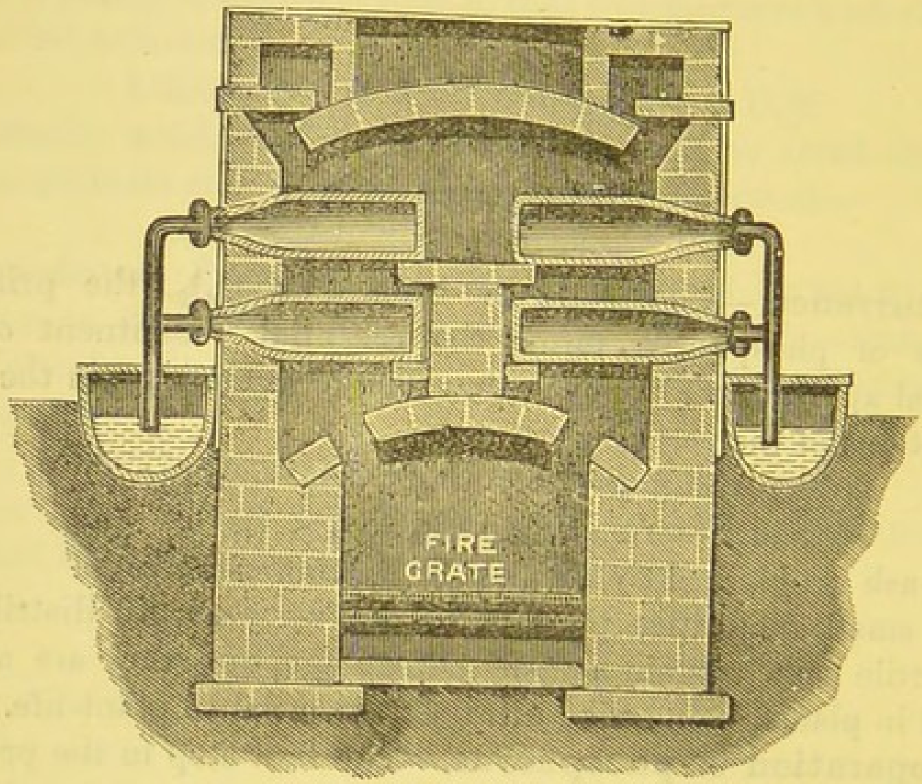


FIG. 16.

water, and filtering through chamois leather or canvas to remove suspended matter, and then finally cast into sticks.

Properties of phosphorus.—The phosphorus so obtained is a yellowish, translucent solid which can be readily cut with a knife. It has a specific gravity of 1·82, it melts at 43° C., and boils at 269° C. It is insoluble in water, but readily dissolves in bisulphide of carbon. It is kept under water, since when exposed to air it slowly oxidizes, and even at 34° C. ignites and burns with great brilliancy. It combines also at ordinary temperatures with fluorine, chlorine, bromine, iodine, and sulphur, and in the finely-divided condition with oxygen, with the evolution of light and heat.

Phosphorus may be obtained in two other allotropic modifications, the red or amorphous phosphorus, and the crystalline form (rhombohedra).

Amorphous phosphorus is, according to its method of preparation, a reddish-brown powder or a close-textured mass showing conchoidal fracture. This form is prepared on the large scale by heating ordinary phosphorus at 250° C. in cast-iron pots from which the air is excluded, and removing the unconverted phosphorus which remains, by boiling the finely-divided product with caustic soda solution. On a small scale in the laboratory it may readily be obtained by heating ordinary phosphorus in an atmosphere of nitrogen or carbon dioxide. The amorphous phosphorus differs very considerably in its properties from that already described. It has a higher specific gravity (2·14), and is insoluble in bisulphide of carbon. It undergoes no change in air at ordinary temperatures, and may be freely handled without danger; it combines with oxygen, the halogens, and sulphur at much higher temperatures than ordinary phosphorus. Unlike ordinary phosphorus, it is not poisonous.

Lucifer matches are tipped with a mixture of phosphorus and certain substances, such as lead dioxide and potassium nitrate, which readily part with oxygen. "Safety" matches contain no phosphorus, being tipped with a mixture of antimony sulphide (Sb_2S_3), the sulphur being the inflammable body, and potassium chlorate; in this case the match is ignited by rubbing it on a prepared surface of red phosphorus and powdered glass. In either case the heat requisite to promote chemical action and to ignite the phosphorus is generated by friction on a rough surface.

Crystalline phosphorus is obtained by heating phosphorus in a sealed tube along with metallic lead and allowing it to cool, subsequently removing the lead by dissolving it in dilute nitric acid.

Hydrides of Phosphorus.

Phosphorus forms three hydrides—

Gaseous phosphoretted hydrogen or phosphine	PH_3.
Liquid phosphoretted hydrogen	P_2H_4.
Solid phosphoretted hydrogen	P_4H_2.

PHOSPHORUS TRIHYDRIDE, PH_3.—This gas, which is the analogue of ammonia, is obtained by heating phosphorus in a flask with a solution of caustic soda. As obtained in this way it is mixed with small quantities of the liquid and solid hydrides which render it spontaneously inflammable in air, the air is therefore, previous to heating, displaced from the apparatus by hydrogen, and the end of the delivery tube must dip under water as shown (Fig. 17). The reaction which takes place is—

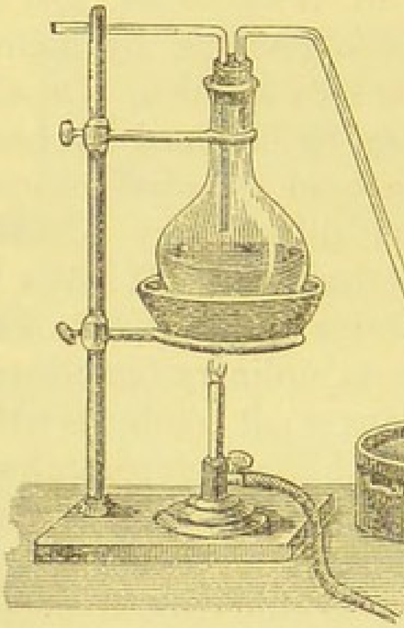


FIG. 17.

$$4\,P + 3\,NaOH + 3\,H_2O = \underset{\text{Sodium hypophosphite.}}{3\,NaH_2PO_2} + PH_3.$$

It is also formed when phosphide of calcium (obtained by heating together lime and phosphorus in a closed crucible) is brought into contact with water.

Properties of PH_3.—It is a colourless gas which condenses only when cooled to − 90° C. It is very slightly soluble in water, and possesses a penetrating garlic-like odour which is evident even with very small quantities of the gas ; it is very poisonous. If free from other hydrides, it is not inflammable in air at ordinary temperatures; heat decomposes the gas into its elements more readily than the corresponding nitrogen compound, NH_3.

Just as ammonia combines directly with the haloid acids HCl, HBr, etc., to form ammonium chloride, ammonium bromide, etc., so phosphorus trihydride forms similar compounds. The combination with hydriodic acid to form phosphonium iodide—

$$PH_3 + HI = PH_4I$$

takes place very readily. This body may be used as a source of *pure* PH_3 by acting upon it with potash or soda, the reaction being analogous to that employed in the preparation of ammonia—

$$PH_4I + NaOH = PH_3 + NaI + H_2O.$$
$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O.$$

Liquid hydride of phosphorus, P_2H_4.—This is obtained when calcium phosphide is acted upon by water at 60°C. If the product be passed through a U-tube surrounded by a freezing mixture the hydride condenses to a clear liquid which takes fire when exposed to air at ordinary temperatures.

Solid hydride of phosphorus, P_4H_2.—This is a yellow bulky powder obtained when the other hydrides are exposed for some time to light or brought into contact with hydrochloric or sulphuric acid. It does not ignite below 200°C.

The Oxides and Oxy-acids of Phosphorus.

Oxides.	Corresponding Acids.	
P_4O		
P_2O (not known in free state)	Hypophosphorus acid,	H_3PO_2 or $3\ H_2O.\ P_2O$.
P_2O_3 (P_4O_6)	Phosphorus acid,	H_3PO_3 or $3\ H_2O.\ P_2O_3$.
P_2O_4	Hypophosphoric acid,	$H_4P_2O_6$ or $2\ H_2O.\ P_2O_4$.
P_2O_5	Orthophosphoric acid,	H_3PO_4 or $3\ H_2O.\ P_2O_5$.
	Pyrophosphoric acid,	$H_4P_2O_7$ or $2\ H_2O.\ P_2O_5$.
	Metaphosphoric acid,	HPO_3 or $H_2O.\ P_2O_5$.

The more important are the phosphorous oxide and the phosphorous pentoxide, and the acids derived from them.

Phosphorus Suboxide, P_4O.—This is the lowest oxide of phosphorus. It is a yellow powder obtained (mixed with other oxides) when phosphorus is oxidized in a limited supply of air or when phosphorus is dissolved in phosphorus trichloride and exposed to light in contact with air.

Hypophosphorus Acid, H_3PO_2.—The oxide corresponding to this acid has not been obtained. The acid is monobasic, only one of the three hydrogen atoms being replaceable by a metal. Sodium hypophosphite is formed when, in the preparation of phosphorus trihydride, phosphorus is acted upon by caustic soda. The free acid is best prepared from barium hypophosphite obtained in the analogous reaction of barium hydrate and phosphorus.

$$3\ Ba(OH)_2 + 8\ P + 6\ H_2O = 3\ BaH_4P_2O_4 + 2\ PH_3$$

Sulphuric acid is added to the barium salt just sufficient to form the insoluble barium sulphate ; the supernatant liquid on evaporation yields the acid in white crystals.

$$BaH_4P_2O_4 + H_2SO_4 = BaSO_4 + 2\ H_3PO_2.$$

The free acid and its alkaline salts are powerful reducing agents and precipitate the metal from solutions of gold, silver, mercury, and some other salts ; with sulphate of copper the product obtained is the hydride of copper.

Phosphorous oxide, P_4O_6.—Phosphorous oxide or anhydride is obtained when phosphorus is exposed to oxidation in air at ordinary temperatures, or when it is burnt in a limited supply of air. This may be effected by placing a small piece of dry phosphorus in a tube drawn out so as to form a fine orifice, the other end of the tube being connected with an aspirator.

The phosphorus is gently warmed, and then a *slow* stream of dry air is drawn through the tube. The phosphorous oxide collects in the tube as a white powder, which on exposure to moist air ignites, forming the higher oxide P_2O_5.

Phosphorous acid, H_3PO_3, is prepared by the action of excess of water on phosphorus trichloride—

$$PCl_3 + 3\ H_2O = H_3PO_3 + 3\ HCl.$$

The hydrochloric acid is easily volatilized by heating the product on a water-bath, phosphorous acid remaining. It is a reducing agent, as it readily takes up oxygen, and is transformed into ordinary phosphoric acid, H_3PO_4.

Phosphorus tetroxide, P_2O_4 is obtained in white crystals when the products of combustion of phosphorus in a limited supply of air are sublimed *in vacuo* at 290° C. The oxide is deliquescent and in presence of moisture passes readily into phosphorous and phosphoric acids :

$$P_2O_4 + 3\ H_2O = H_3PO_3 + H_3PO_4.$$

PHOSPHORUS PENTOXIDE, P_2O_5.—Whenever phosphorus is burnt in an excess of dry oxygen or air this oxide is formed. The operation may be performed in a glass bolt-head with two side tubes, through one of which passes air dried over fused calcium chloride, and through the other the fumes are aspirated, a bottle being placed between the aspirator and the side tube to intercept the phosphorus pentoxide (Fig. 18). A small piece of phosphorus carefully dried between filter paper is introduced through the neck of the bolt-head into a small basin attached as shown, and then successively other pieces, until sufficient of the oxide has been prepared. After the first piece has been ignited by touching it with a hot wire, the basin will be hot enough to start the combustion of the subsequent portions as they are dropped into it. The pentoxide so obtained always contains phosphorous oxide, from which it may be freed by passing it in the gaseous form along with oxygen over gently heated finely divided platinum. Compare preparation of sulphur trioxide.

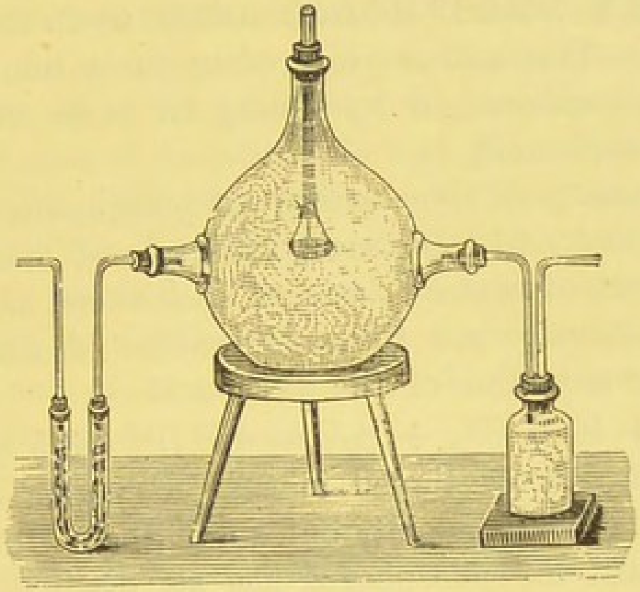


FIG. 18.

Properties of P_2O_5.—The oxide is an amorphous white powder, which when left in contact with moist air gradually absorbs moisture and deliquesces. When thrown into water it combines with it with a hissing noise, and forms metaphosphoric acid, HPO_3.

$$P_2O_5 + H_2O = 2\ HPO_3.$$

Its great affinity for water renders it a valuable agent for completely drying gases, whilst in contact with acids it frequently deprives them of water, forming anhydrides—

$$H_2SO_4 + P_2O_5 = 2\,HPO_3 + SO_3.$$
$$2\,HNO_3 + P_2O_5 = 2\,HPO_3 + N_2O_5.$$

Similarly it chars wood, paper, and many organic substances by its dehydrating action.

ORDINARY PHOSPHORIC ACID, or **Orthophosphoric Acid, H_3PO_4.**—This acid is prepared by the action of nitric acid on ordinary phosphorus, or by boiling for some time a solution of metaphosphoric acid.

If a few pieces (say 10 grammes) of phosphorus be introduced into a large retort, and 150 c.c. of a mixture of one part of nitric acid to two parts of water be poured upon them, and the mixture be heated cautiously, red fumes of oxides of nitrogen will be evolved by the reduction of the nitric acid—

$$4\,P + 10\,HNO_3 + H_2O = 4\,H_3PO_4 + 5\,N_2O_3$$

If the heating is continued in such a manner as to keep the liquid about its boiling-point, but so that as little as possible distils over until the phosphorus has all disappeared, and red fumes are no longer generated, the acid can then be distilled over until that remaining has a syrupy consistency, more red fumes being evolved at this stage through the oxidation of some phosphorous acid. Finally, the thick liquid can be transferred to a porcelain dish and evaporated so long as strongly acids fumes (HNO_3) are given off.

As trichloride of phosphorus when treated with excess of water yields phosphorous acid, so the pentachloride, by similar treatment, gives ordinary phosphoric acid—

$$PCl_5 + 4\,H_2O = H_3PO_4 + 5\,HCl.$$

Phosphoric acid, when sufficiently concentrated, crystallizes on standing; it is a tribasic acid, each of the atoms of hydrogen being replaceable by a metal.

The phosphates.—The phosphates of the alkalies, sodium, potassium, and ammonium, are soluble in water, and are obtained by the addition in solution of the alkaline hydrates to phosphoric acid. The amount of the alkali added may be sufficient to replace one, two, or three atoms of the hydrogen, thus—

$$\underset{40}{NaOH} + \underset{98}{H_3PO_4} = NaH_2PO_4 + H_2O.$$

$$\underset{80}{2\,NaOH} + \underset{98}{H_3PO_4} = Na_2HPO_4 + 2\,H_2O.$$

$$\underset{120}{3\,NaOH} + \underset{98}{H_3PO_4} = Na_3PO_4 + 3\,H_2O.$$

The numbers underneath show the combining proportions of caustic soda and phosphoric acid required to form such salts. That is to say, if to 98 grammes of phosphoric acid there be added 40 grammes of caustic soda and the solution evaporated the salt NaH_2PO_4 will be obtained; if 80 grammes, then the salt formed will be Na_2HPO_4, and if 120 grammes, the salt Na_3PO_4 will be formed. The salt in which the whole of the hydrogen is replaced is known as the *normal* salt, and we have here an instance of a normal salt which is not neutral in its reaction with litmus but alkaline.

NaH_2PO_4, Sodium dihydrogen phosphate—acid reaction.
Na_2HPO_4, Disodium hydrogen phosphate—slightly alkaline.
Na_3PO_4, Normal sodium phosphate—distinctly alkaline.

In "microcosmic salt" part of the hydrogen is replaced by sodium and part by ammonium, $Na.NH_4.HPO_4$.

The normal phosphates of the alkaline earths (Ba, Sr, Ca) and of Mg, Pb, Ag, and indeed of all the other metals, are insoluble in water, but soluble in dilute mineral acids. They may be prepared by adding a soluble salt of the metal in question to an aqueous solution of an alkaline phosphate—

$$2\,Na_3PO_4 + 3\,CaCl_2 = Ca_3(PO_4)_2 + 6\,NaCl.$$

$$Na_3PO_4 + 3\,AgNO_3 = Ag_3PO_4 + 3\,NaNO_3.$$

Tests for phosphates.—(1) Ferric chloride gives, even in presence of acetic acid, a yellowish-white precipitate of ferric phosphate. (Arsenates also give a yellowish-white precipitate.)

(2) Silver nitrate gives a pale yellow precipitate of silver phosphate. (Arsenates give a brick-red precipitate.)

(3) Excess of ammonium molybdate in the presence of nitric acid gives a bright yellow precipitate of phospho-molybdate of ammonium even in the cold, but more rapidly on warming. (The arsenates give a similar precipitate only on warming.)

(4) The presence of phosphorus may always be detected by heating a little of the powdered substance along with magnesium filings in a narrow tube and then moistening the product with water. Phosphoretted hydrogen is given off, and may be recognized by its characteristic odour.

Pyrophosphoric acid, $H_4P_2O_7$, is obtained by heating ordinary phosphoric acid to 300° C.

$$2\ H_3PO_4 = H_4P_2O_7 + H_2O.$$

As with the phosphates, the salts of the alkali metals are soluble in water, those of the other metals being insoluble in water but soluble in dilute mineral acids.

Tests for pyrophosphates.—(1) Silver nitrate gives a *white* precipitate of the pyrophosphate, thus distinguishing it from the phosphate.

(2) Pyrophosphoric acid does not coagulate albumen.

Metaphosphoric acid, HPO_3, is obtained when ortho- or pyrophosphoric acid or their ammonium salts are strongly heated—

$$H_3PO_4 = HPO_3 + H_2O.$$

Like the pyrophosphates they give a *white* precipitate with silver nitrate, but metaphosphoric acid is distinguished by the fact that it coagulates albumen.

Compounds of phosphorus with the halogens.—By direct union of phosphorus with these elements, bodies of the type PX_3 and PX_5 are formed, and by the action of moisture on PCl_5 and PBr_5, the oxychlorides $POCl_3$, and oxybromides $POBr_3$, respectively, are formed.

Chlorides of Phosphorus, PCl_3 and PCl_5.

When phosphorus burns in dry chlorine, phosphorus trichloride, PCl_3, is formed as a colourless fluid whose boiling-point is 73° C., and if excess of chlorine be present the trichloride is gradually transformed into the pentachloride, PCl_5. This is a yellowish solid substance which passes directly into vapour at 168° C., without melting, undergoing partial decomposition into PCl_3 and Cl_2.

In presence of moisture, PCl_5 slowly changes into a fuming liquid, phosphorus oxychloride, $POCl_3$—

$$PCl_5 + H_2O = POCl_3 + 2\ HCl.$$

Phosphorus trichloride under similar circumstances forms phosphorous acid—

$$PCl_3 + 3\ H_2O = H_3PO_3 + 3\ HCl.$$

This tendency to combine with oxygen and liberate chlorine renders these chlorides valuable reagents for substituting chlorine for oxygen or hydroxyl (OH), in this latter case eliminating HCl. The following equations represent some of the more important reactions illustrating this—

$$SO_3 + PCl_3 = POCl_3 + SO_2.$$

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

$$SO_2 \left\{ \begin{matrix} OH \\ OH \end{matrix} \right. + PCl_5 = POCl_3 + SO_2 \left\{ \begin{matrix} OH \\ Cl \end{matrix} \right. + HCl.$$

$$SO_2 \left\{ \begin{matrix} OH \\ Cl \end{matrix} \right. + PCl_5 = POCl_3 + SO_2Cl_2 + HCl.$$

$$\underset{\text{Ethyl alcohol.}}{C_2H_5OH} + PCl_5 = POCl_3 + \underset{\text{Ethyl chloride.}}{C_2H_5.\ Cl} + HCl.$$

$$\underset{\text{Acetic acid.}}{C_2H_3O.\ OH} + PCl_5 = POCl_3 + \underset{\text{Acetyl chloride.}}{C_2H_3O.\ Cl} + HCl$$

$$\underset{\text{Aldehyde.}}{CH_3CHO} + PCl_5 = POCl_3 + \underset{\text{Ethylidene chloride.}}{CH_3CHCl_2.}$$

By the action of an *excess* of water on phosphorus pentachloride orthophosphoric acid is formed, the whole of the chlorine being eliminated as hydrochloric acid—

$$PCl_5 + 4\ H_2O = H_3PO_4 + 5\ HCl.$$

CHAPTER VII.

SILICON AND BORON.

Occurrence.—Silicon, occurring in combination with oxygen as silica (SiO_2), is widely distributed, and forms the predominant constituent of many minerals and rocks. Quartz, agate, and kieselguhr (a finely-divided siliceous material of organic origin) are essentially pure silica, whilst sandstone must be regarded as silica associated with varying quantities of oxide of iron, or alumina. Shale or clay consists of silica and alumina in more or less definite proportions, and a large body of mineral silicates of common occurrence, such as felspar, serpentine, steatite, are very rich in silica. The element silicon is not found in the free state, and is not easy to isolate from its compounds, so that although it constitutes nearly one-fourth of the mass of the earth's crust, it is yet a substance rarely met with even in the laboratory.

Preparation and properties of silicon.—Silicon is obtained by the action of sodium, potassium, or aluminium on silicon tetrachloride ($SiCl_4$), or on potassium silico-fluoride (K_2SiF_6), in an atmosphere of hydrogen, or under such other conditions as to exclude oxidation—

$$SiCl_4 + 4\,K = 4\,KCl + Si.$$

$$K_2SiF_6 + 4\,K = 6\,KF + Si.$$

The residue is washed free from the potassium salts, which are readily soluble in water, and the silicon remains usually as a brown, amorphous powder.

A crystalline modification of silicon is also obtained under certain conditions, and has in its colour and lustre a considerable resemblance to graphite. Silicon also resembles carbon in that it can be burnt in oxygen (to form the dioxide, silica) and at ordinary temperatures fluorine is the only element which combines with it directly. Acids (except HF) have no action upon it.

Silicon hydride, SiH_4.—By heating together metallic sodium and potassium silicofluoride (after the manner requisite to obtain silicon) in presence of *anhydrous* magnesium chloride, an alloy of magnesium and silicon is obtained. This, on treatment with hydrochloric acid, forms the hydride, SiH_4, a gaseous body, analogous to marsh gas, CH_4. This compound is not very stable, and decomposes at a red heat into amorphous silicon and hydrogen. In presence of oxygen or chlorine it takes fire spontaneously, forming silica and silicon tetrachloride respectively.

Silicon fluoride, SiF_4, is obtained by the direct union of silicon and fluorine at the ordinary temperature, or by the action of hydrofluoric acid on silica or a silicate—

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

If an intimate mixture of about 10 grammes of silica or fine white sand, with twice its weight of calcium fluoride or finely-powdered fluorspar, be introduced into a *dry* 8-ounce flask, fitted with a cork and delivery-tube, as shown in the figure, and enough

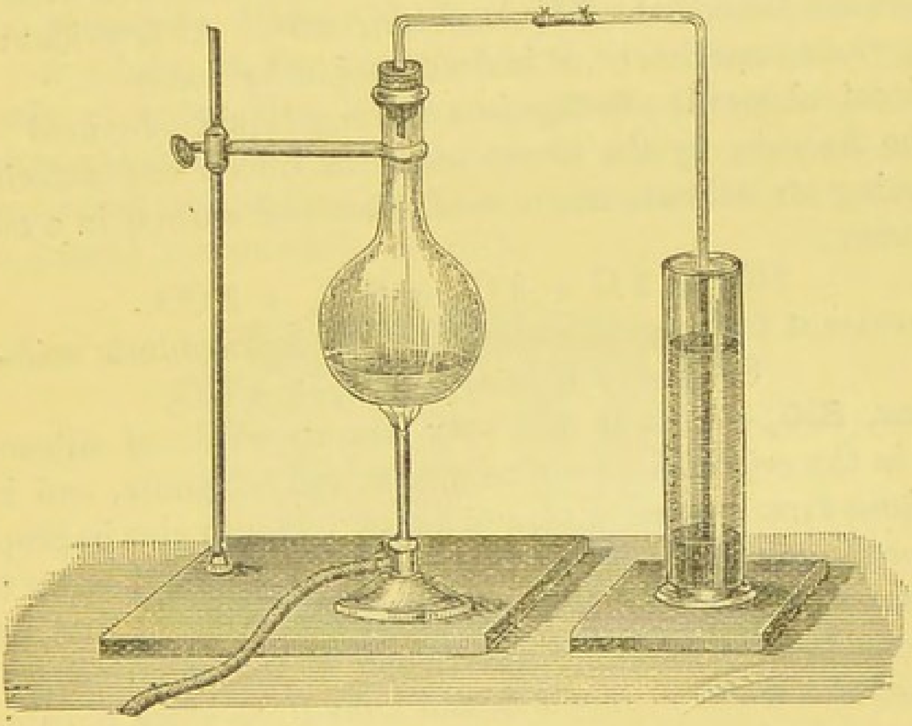


FIG. 19.

concentrated sulphuric acid to form a thin paste be poured on it, on gently heating, silicon fluoride will be given off. If the gas be passed into water (50 c.c.), gelatinous silica separates out and a solution of hydrofluosilicic acid is formed—

$$3\,SiF_4 + 4\,H_2O = H_4SiO_4 + 2\,H_2SiF_6.$$

In order to prevent the delivery-tube becoming stopped by the gelatinous silica, a little mercury may be poured into the cylinder, and the delivery-tube arranged so that it just dips below the surface of this. If, after the gas has been passed for some minutes, some of the clear liquid is poured off, its acid reaction may be shown by means of litmus paper. Add potassium carbonate and carbon dioxide is given off with effervescence, whilst a fine white powder will separate out, consisting of potassium silicofluoride, K_2SiF_6, one of the most insoluble of the salts of potassium. The gelatinous silica may be washed by decantation.

Silicon fluoride is a colourless gas which fumes in moist air, and has an irritant effect on the mucous membrane, even more pronounced than that of hydrochloric acid. As is evident from the previous experiment, it is decomposed by water.

Silicon chloride, $SiCl_4$, is a fuming liquid obtained either like the fluoride, by the direct union of silicon and chlorine, or by heating an intimate mixture of silica and carbon in a current of chlorine;

$$SiO_2 + 2\,C + 2\,Cl_2 = SiCl_4 + 2\,CO.$$

With water it forms gelatinous silica and hydrochloric acid—

$$SiCl_4 + 4\,H_2O = H_4SiO_4 + 4\,HCl.$$

Silica, SiO_2.—This is the only known oxide of silicon. It occurs in the *crystalline* form as quartz and tridymite, and in the *amorphous* form as opal, flint, and agate. It may also be prepared from certain mineral silicates, or silicates of the alkalies, by treating them with hydrochloric acid. It separates at first in the gelatinous form containing water, and if this gelatinous silica be heated the water is expelled, and anhydrous silica remains.

In the anhydrous condition, or in the mineral form, silica is unattacked by acids, with the exception of hydrofluoric acid; it can, however, be brought into solution again by fusion with alkaline carbonates.

If some silica and about four times its weight of potassium carbonate be mixed together and heated in a platinum crucible over the flame of a Bunsen burner, the mass swells up and evolves large quantities of carbon dioxide—

$$\underset{}{K_2CO_3} + SiO_2 = \underset{\text{Potassium Silicate.}}{K_2SiO_3} + CO_2.$$

If, after heating for about half-an-hour, the mass is allowed to cool, and extracted with water, any insoluble matter (unattacked silica) which remains being filtered off, the solution contains potassium silicate, together with potassium carbonate, which has been used in excess. If strong hydrochloric acid be added to the solution until a marked acid reaction is obtained, and the solution be sufficiently concentrated, a flocculent precipitate of silica will be obtained. If, however, the solution be dilute, no immediate precipitate is obtained, though one may separate on standing or by boiling.

The solution contains potassium chloride, free hydrochloric acid, and silica, and from such a solution a *soluble* form of silica may be prepared. Make a shallow dish by binding parchment paper over a hoop of tin or gutta-percha, float this on a considerable body of water (Fig. 20), and pour the liquid into it. The potassium chloride and hydrochloric acid will slowly pass through the membrane and diffuse into the water, while the silica will remain behind in solution in the dish.

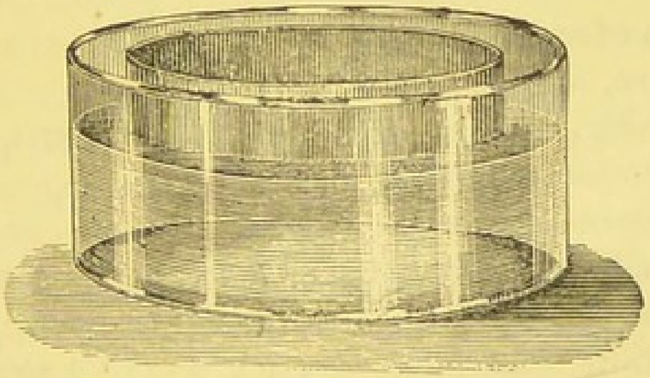


FIG. 20.

Sugar, salt, and such bodies behave like potassium chloride, and readily pass through such a membrane, whilst white of egg, caramel, and the like, only do so extremely slowly. The former, from the fact that they are mostly crystallizable bodies, have been termed *crystalloids*, and the latter, from their gelatinous and amorphous nature, *colloids*. Silica is a colloid, and by means of this experiment it may be separated from such substances as common salt and potassium chloride, and obtained in solution. Under these circumstances we obtain silica in a form in which it is soluble in water.

There is, however, a third modification intermediate between these two, for when silica is freshly precipitated *in the cold*, it may be redissolved by the addition of dilute hydrochloric acid.

On standing, and more rapidly when boiled, this form becomes much less soluble, and ultimately passes into the insoluble variety.

To sum up we have—

(1) Mineral silica (crystalline or amorphous) and anhydrous silica insoluble in and unattacked by the ordinary acids, with the exception of hydrofluoric acid.

(2) Gelatinous silica, soluble in dilute acids.

(3) Dialyzed silica, soluble in water.

Gelatinous silica when dried at the ordinary temperature retains water, and has approximately the composition SiO_2, $2\ H_2O$, or H_4SiO_4, usually known as orthosilicic acid.

The silicates.—These salts are chiefly interesting from the fact that they are largely represented in the mineral kingdom; the following list indicates some of those of more common occurrence—

(1) Silicates of magnesium.

Olivine, Mg_2SiO_4, or $2\ MgO.\ SiO_2$.
Talc, $Mg_3H_2Si_4O_{12}$, or $3\ MgO.\ H_2O.\ 4\ SiO_2$.
Serpentine, $Mg_3Si_2O_7$, or $3\ MgO.\ 2\ SiO_2$.

(2) The Felspars.

Orthoclase, $K_2Al_2Si_6O_{16}$, or $K_2O.\ Al_2O_3.\ 6\ SiO_2$.
Albite, $Na_2Al_2Si_6O_{16}$, or $Na_2O.\ Al_2O_3.\ 6\ SiO_2$.
Anorthite, $CaAl_2S_2O_8$, or $CaO.\ Al_2O_3.\ 2\ SiO_2$.

and the decomposition product of the felspars—

Kaolin, $H_2Al_2Si_2O_8$, or $H_2O.\ Al_2O_3.\ 2\ SiO_2$.

A glance at this list is sufficient to show that the composition of the silicates is often very complex. With the exception of those of the alkalies they are all practically insoluble in water, and for the most part they can only be brought into solution either by treatment with hydrofluoric acid or by fusion with alkaline carbonates.

BORON.

Occurrence.—Boron is chiefly derived from native borax ($Na_2B_4O_7 . 10\ H_2O$), obtained by the condensation of steam issuing from the ground in certain parts of Tuscany. It is also found in combination with lime as calcium borate, the mineral borocalcite, $CaB_4O_7 . 4\ H_2O$, and as boracite, $2\ Mg_3B_8O_{15} . MgCl_2$.

Boron is obtained by reducing its oxide, B_2O_3, by means of sodium, potassium, or magnesium—

$$B_2O_3 + 6\ Na = 3\ Na_2O + 2\ B.$$

It is thus prepared in the *amorphous* condition as a brown powder, which is very difficult to fuse and not readily oxidized. Like other non-metals, it is a bad conductor of electricity.

When mixed with aluminium, exposed to a white heat and allowed to cool, the *crystalline* form of boron is obtained, the aluminium being removed by treatment with caustic soda. Prepared in this way it is, however, always associated with small quantities of carbon and aluminium.

Boron hydride, BH_3, is a gaseous body which burns with a green-mantled flame, and is decomposed into its elements at a red heat. In order to obtain it, magnesium boride, Mg_3B_2, is first prepared by heating together magnesium and boric acid, and this is then treated with hydrochloric acid. It has, however, not been obtained in a state of purity, being always associated with free hydrogen.

Boron trichloride, BCl_3.—Amorphous boron combines directly without the application of heat with chlorine. The trichloride may also be prepared by a method similar to that used for silicon tetrachloride, viz. by passing chlorine over an intimate mixture of the trioxide with carbon at a high temperature—

$$B_2O_3 + 3\ C + 3\ Cl_2 = 2\ BCl_3 + 3\ CO.$$

It is a colourless liquid which fumes in air, and is readily decomposed by water, forming the trioxide and hydrochloric acid—

$$2\ BCl_3 + 3\ H_2O = B_2O_3 + 6\ HCl.$$

In the anhydrous condition it is, however, very stable, and may even be distilled in contact with sodium without decomposition.

Fluorine combines energetically at ordinary temperatures with boron, and bromine can also be made to combine directly with it, forming the trifluoride and tribromide respectively. Nitrogen also combines directly with it, forming the nitride, BN.

Boron trioxide, B_2O_3.—This and the boric acid and borates derived from it are the most important of the boron compounds. The oxide is formed when boron is burnt in air, but is usually prepared by heating boric acid—

$$2\ H_3BO_3 = B_2O_3 + 3\ H_2O.$$

Water is driven off and there remains a glassy-looking mass which when powdered combines slowly with water, forming boric acid (H_3BO_3) again.

Boric acid and the borates.—Boric acid is a very weak acid which, like carbonic acid, gives with litmus a wine-red colour quite distinct from the bright red resulting from such acids as hydrochloric and sulphuric.

If concentrated hydrochloric acid be added to a strong hot solution of borax ($Na_2B_4O_7$) the acid is set free and separates out in thin laminæ—

$$Na_2B_4O_7 + 2\ HCl + 5\ H_2O = 4\ H_3BO_3 + 2\ NaCl.$$

The borates, with the exception of those of the alkalies, are only slightly soluble in water. When mixed with concentrated sulphuric acid and gently heated at the border of the Bunsen flame they impart a green colour to it, owing to the volatilization of free boric acid. A similar colouration is also obtained when alcohol is added to such a mixture and ignited. These properties may be used as the means of detecting the presence of borates. When borax is fused on a platinum wire along with small quantities of chromium, cobalt, copper, manganese, or other compounds, characteristic colours are imparted to it.

CHAPTER VIII.

THE ALKALIES.

K, (Am) Na.

General Characters.—

1. The elements of this group are monovalent and replace the hydrogen in the acids atom by atom, forming normal and acid salts, *e. g.*—

From HCl, salts of the type RCl
„ H_2SO_4, „ „ „ R_2SO_4 and $RHSO_4$
„ H_3PO_4, „ „ „ R_3PO_4, R_2HPO_4, RH_2PO_4

2. The metals are soft and malleable, they decompose water at the ordinary temperature and form strongly basic hydroxides—

$$2\ R + 2\ H_2O = 2\ ROH + H_2.$$

Also they undergo oxidation when exposed to air at ordinary temperatures.

3. The metals combine directly with hydrogen when heated in it, forming *hydrides* of the general composition R_4H_2.

4. Under the action of dry ammonia they form *amides* of the composition RNH_2, which on heating are transformed into *nitrides* of the composition R_3N.

5. The binary compounds of this group (haloid salts, oxides, and sulphides) show a considerable tendency to attach more than the normal amount of the electronegative element. Such compounds are—

(*a*) the peroxides, R_2O_2, R_2O_3, R_2O_4, and persulphides.

(*b*) the trihalides and pentahalides RCl_3, RCl_5, RI_3, RI_5, RCl_2I, RCl_4I, etc.

6. The normal carbonates are stable at high temperatures (except ammonium carbonate).

POTASSIUM.

Occurrence.—Potash occurs in combination chiefly with alumina and silica in the older rocks as potash felspar (orthoclase) $K_2O.Al_2O_3.6\,SiO_2$, potash mica (muscovite) $K_2O.3\,Al_2O_3$ $4\,SiO_2$, and in other mineral silicates. It is also found locally in the neighbourhood of Stassfurt as Carnallite $KCl.MgCl_2.6\,H_2O$, in East Galicia as Sylvine, KCl, and as nitrate in the form of an efflorescence on the soil in the rainless districts of Peru, Chili, etc.

The ash of plants contains a notable quantity of potassium salts, chiefly carbonate, which may be extracted by water. Almost the whole of the potash salts used to be obtained in this way, and from the fact of their being extracted by boiling their ash in pots the salts were termed "Pot-ashes" (hence *potash*), a more refined product being called "pearl-ash." In more recent times the residues from the manufacture of beetroot sugar have been employed as a source of potassium salts, the liquors being evaporated and calcined; a product is thus obtained which contains about 60 per cent. of potassium salts. The washings of sheeps' wool ("suint") by similar treatment yield a residue containing about 90 per cent. of potassium salts. The ashes from "kelp" were formerly largely extracted, but now are employed to a smaller extent, and only crude salts are prepared from them. By far the most important source of potassium salts are the mines at Stassfurt, where over 100,000 tons of the chloride are annually produced.

Metal.—This was first obtained by Davy in 1807 by the electrolytic decomposition of fused caustic potash. It was afterwards prepared on a larger scale by Gay Lussac and Thénard by strongly heating caustic potash in contact with metallic iron.

The method generally adopted however is that of heating an intimate mixture of potassium carbonate and carbon (obtained by igniting crude potassium tartrate in a closed vessel) in cylindrical iron retorts placed horizontally, as shown in Fig. 21. The principal reaction is

$$K_2CO_3 + 2\,C = 2\,K + 3\,CO.$$

The carbonic oxide and vapours of potassium pass off by the tube into a receiver which presents a large area for cooling. The receiver, as shown in the figure, is made up of two flat plates screwed together so as to leave a narrow space between them, and

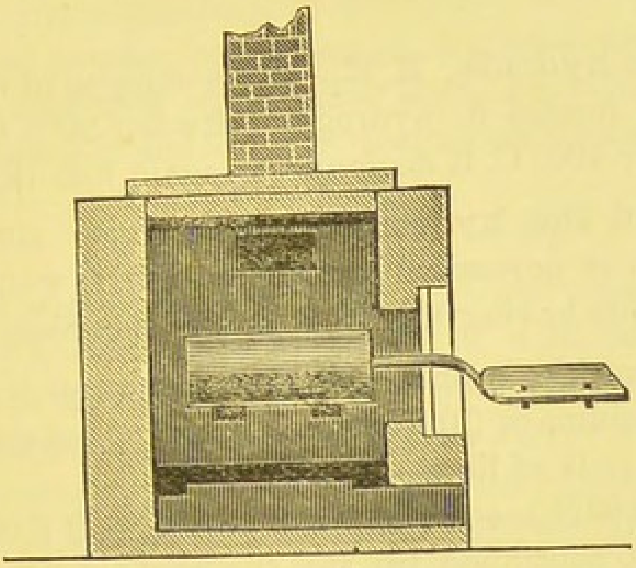


FIG. 21.

the potassium condenses between these and is periodically removed and preserved in petroleum.

The process of Castner, which is in principle that originally used by Gay Lussac and Thénard, is also employed. Carbide of iron is first prepared by heating pitch with finely divided iron (obtained by the reduction of the oxide). This is mixed with caustic potash and heated in steel crucibles; a large amount of hydrogen and carbonic oxide is evolved, and ultimately the metallic potassium is distilled off. It is also, like sodium (see page 112), prepared on the large scale by the electrolysis of caustic potash, the process being a continuous one.

Potassium is a soft metal with a silvery lustre; has a sp. gr. of 0·875, and is lighter than sodium; it melts at 62° C. and boils at a dull red heat, forming a green vapour, whose density is 19. Though not acted upon by perfectly dry oxygen it rapidly tarnishes by oxidation in moist air even at ordinary temperatures. It likewise combines directly with hydrogen and the halogens and with sulphur, selenium and phosphorus when heated. It decomposes water at ordinary temperatures according to the equation

$$2\,K + 2\,H_2O = 2\,KOH + H_2$$

and almost all oxides undergo a partial or complete reduction if they are heated in contact with potassium. K and Na in the proportions K_2Na form an alloy which is liquid at ordinary temperatures.

Potassium hydride, K_4H_2.—This compound is formed when potassium is heated in hydrogen between 200° C. and 400° C.; at a little over 400° C. it decomposes again into its elements.

Oxides and the hydroxide.—The oxide corresponding to caustic potash or potassium hydroxide (KOH) would be K_2O, but no definite oxide having this composition has been prepared.

The Hydroxide is obtained (1) when water is acted upon by metallic potassium, or (2) when a solution of potassium carbonate is boiled with milk of lime—

$$Ca(OH_2) + K_2CO_3 = 2\ CaCO_3 + 2\ KOH.$$

The boiling is continued till the supernatant liquid no longer effervesces when dilute acid is added to it. The calcium carbonate is then settled out and the clear liquid decanted off and boiled down to expel water until it is found to solidify on cooling. It usually contains as impurities, alumina, silica and carbonates of calcium and potash; these are all insoluble in alcohol, whilst potash is freely soluble. By shaking up the potash with alcohol the impurities are left undissolved, and can be allowed to settle; if the clear solution is boiled down in a silver basin, pure potash is left behind.

Caustic potash may also be obtained by the double decomposition of the sulphate with barium hydrate—

$$K_2SO_4 + Ba(OH)_2 = 2\ KOH + BaSO_4.$$

The barium sulphate is an insoluble heavy powder which may be readily settled out.

Caustic potash is, as its name implies, strongly caustic and acts very powerfully on animal and vegetable tissue; when exposed to air it readily takes up carbon dioxide forming the carbonate. Other gases, as for instance SO_2, Cl and H_2S and the oxides of nitrogen, are also taken up by it, so that it is often of service for the removal of such gases when they occur as impurities. It is one of the most active bases, and from it most of the salts of potassium may be prepared by the addition of an equivalent amount of the corresponding acid.

By gradual heating of potassium in air or oxygen it passes into the *dioxide* K_2O_2, a white powder which however readily takes up more oxygen and ultimately on prolonged heating passes into a chrome yellow powder consisting of the *tetroxide*, K_2O_4. They are powerful oxidizing agents, and K_2O_4 when heated in carbon monoxide oxidizes it and forms potassium carbonate, oxygen being also given off—

$$K_2O_4 + CO = K_2CO_3 + O_2.$$

Sulphides and hydrosulphide.—When potassium sulphate is reduced by heating it in hydrogen or with carbon the *monosulphide* K_2S is obtained. This is a pale yellow powder, which however contains small quantities of the higher sulphides; when dissolved in water or when a solution of caustic potash is acted upon by sulphuretted hydrogen, the *hydro-sulphide* KHS is obtained. The higher sulphides K_2S_2, K_2S_3 K_2S_4 and K_2S_5 are darker in colour the more sulphur they contain; they may be prepared by fusing potash and sulphur together (*liver of sulphur*, a mixture of these sulphides, is thus obtained) or by dissolving sulphur in the hydrosulphide.

Potassium hydrosulphide (like AmHS) dissolves the sulphides of arsenic, antimony, tin, platinum, gold and molybdenum, forming sulpho-salts, *e. g.*—

$$2\,KHS + As_2S_3 = \underset{\text{Potassium Sulpharsenite.}}{K_2S.As_2S_3 \text{ (or } K_2As_2S_4)} + H_2S.$$

In this way such sulphides may be separated from those of copper, lead, mercury, bismuth, and cadmium, which are insoluble in KHS.

Potassium nitride, K_3N.—Potassium dissolves in anhydrous liquid ammonia, forming KNH_3, which gradually loses hydrogen, yielding *potassamide*, KNH_2. When this body is heated, the following change takes place—

$$3\,KNH_2 = K_3N + 2\,NH_3,$$

the nitride being thus obtained.

Potassium fluoride, KF, is prepared by adding potassium carbonate to hydrofluoric acid till it is almost neutral, and then evaporating to dryness. If only half this amount of potassium carbonate be added, the acid fluoride KF.HF is obtained; this substance is used as the source of pure dry HF, which it gives off when heated to redness.

Potassium chloride, KCl, is formed by direct union of the elements, or by neutralizing caustic potash by means of hydrochloric acid. Like sodium chloride, it crystallizes in the anhydrous condition in cubes. It is less soluble than sodium chloride at low temperatures, and much more soluble at higher temperatures (see Fig. 22). Hence if a saturated solution containing both chlorides is gradually cooled down, the potassium chloride crystallizes out first, and in this way the two chlorides are separated from one another on the large scale.

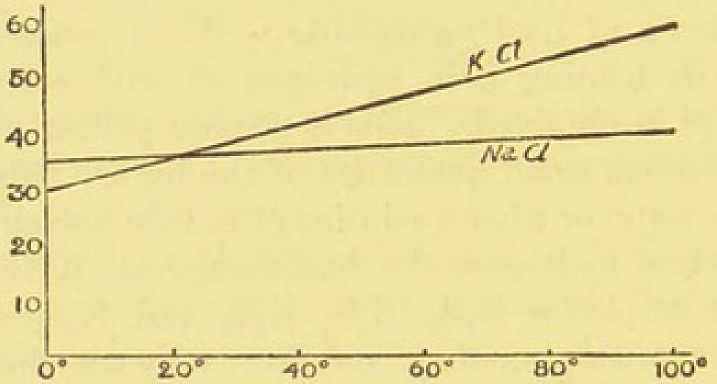


FIG. 22.

Potassium bromide, KBr, is more readily soluble in water than the chloride; it may be obtained by adding hydrobromic acid to the hydroxide or carbonate, or better by mixing together warm solutions of potassium carbonate and bromide of iron. Ferrous carbonate is precipitated, and potassium bromide obtained from the supernatant liquor by evaporation—

$$FeBr_2 + K_2CO_3 = FeCO_3 + 2\ KBr.$$

Potassium iodide, KI, is obtained by similar methods to those employed for the bromide. This is the only potassium salt which has been vaporized without decomposition; a determination of vapour density at a bright red heat gave a value corresponding to the formula KI. Potassium iodide is freely soluble in water and in alcohol, and its solutions dissolve iodine. At 20° C., 100 pts. of water dissolve 35, 65 and 144 pts. of KCl, KBr and KI respectively.

Chlorine water sets free the halogen element from bromide and iodide of potassium—

$$2\ KI + Cl_2 = 2\ KCl + I_2.$$

If a concentrated solution of potassium iodide be saturated with iodine and left over sulphuric acid, dark blue needles of the triiodide, KI_3, separate out.

Potassium cyanide, KCy.—This salt is obtained by heating an intimate mixture of potassium carbonate and nitrogenous organic matter, and extracting the mass with water. In aqueous solution, however, it readily decomposes, and also owing to its great solubility it is difficult to obtain it therefrom in the crystalline condition. It is usual under these circumstances to prepare first the easily crystallizable potassium ferrocyanide, K_4FeCy_6, by the addition of iron to the melt described above. Potassium cyanide is then obtained by strongly heating the ferrocyanide—

$$K_4FeCy_6 = 4\ KCy + FeCy_2.$$

The cyanide fuses, and can be poured off from the residual ferrous cyanide, or the iron and carbon which result from its decomposition.

Potassium hypochlorite, KClO, is only known in solution ; it is prepared by acting on a solution of caustic potash with chlorine *in the cold*—

$$2\ KOH + Cl_2 = KClO + KCl + H_2O.$$

The readiness with which it undergoes decomposition with the production of the free acid (HClO) or chlorine, explains the activity of this salt as a powerful oxidizing or bleaching agent.

Potassium chlorate, $KClO_3$.—When chlorine is passed into a *hot* solution of caustic potash, potassium chlorate is formed, together with chloride, according to the equation—

$$6\ KOH + 3\ Cl_2 = KClO_3 + 5\ KCl + 3\ H_2O.$$

The employment of so large a quantity of the expensive potassium salt, and the difficulty of recovering it, has led to the adoption of a modification of the method, where potassium chlorate is prepared on the large scale.

This consists in the formation of calcium chlorate, by saturating a warm mixture of lime and water with chlorine, the reaction being similar to that with potash—

$$6\ Ca(OH)_2 + 6\ Cl_2 = Ca(ClO_3)_2 + 5\ CaCl_2 + 6\ H_2O.$$

The liquid, after being allowed to settle, is run off and concentrated somewhat by evaporation; potassium chloride in slight excess of the equivalent for $Ca(ClO_3)_2$ is added, and a double decomposition takes place—

$$Ca(ClO_3)_2 + 2\ KCl = 2\ KClO_3 + CaCl_2.$$

The potassium chlorate is much less soluble than the calcium chloride, so that on further concentration and careful cooling, crystals of potassium chlorate separate. This is then purified by recrystallization.

Potassium chlorate is used for the preparation of oxygen, and is, in presence of mineral acids, a powerful oxidizing agent; it is also largely employed in the manufacture of matches and in pyrotechny.

Potassium perchlorate, $KClO_4$.—This is the most stable of this series of salts. It is not decomposed by concentrated hydrochloric acid, while potassium chlorate is readily acted upon with the formation of euchlorine. Also, though strong sulphuric acid acts upon the chlorate with the evolution of the explosive chlorine peroxide, ClO_2, potassium perchlorate when heated with strong sulphuric acid gives rise to the formation of free perchloric acid ($HClO_4$), which distils over—

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

Potassium perchlorate is obtained (with chloride) by heating potassium chlorate until the salt becomes pasty.

$$2\ KClO_3 = KClO_4 + KCl + O_2.$$

Any chlorate which remains may be decomposed by warming with concentrated hydrochloric acid, which is without action on the perchlorate; the chloride is much more soluble in water than the perchlorate, so that the latter may be readily separated by crystallization.

Potassium sulphate, K_2SO_4, is found in the neighbourhood of Stassfurt in the mineral kainite, $K_2SO_4.\ MgSO_4.\ MgCl_2.\ 6\ H_2O$, from which it can be obtained by fractional crystallization. Magnesium chloride remains in the mother liquors, and a hot saturated solution of the crystals, $K_2SO_4.MgSO_4$, which separate, is digested with solid potassium chloride, when the following reaction takes place—

$$K_2SO_4.MgSO_4 + 3\ KCl = 2\ K_2SO_4 + KCl.MgCl_2.$$

The potassium sulphate crystallizes much more readily than the potassium magnesium chloride, and may thus be easily separated from the liquid.

Potassium sulphate is also made by the action of sulphuric acid on the chloride, after a manner similar to that employed on the larger scale for sodium sulphate; it is chiefly used in agriculture.

Potassium hydrogen sulphate, $KHSO_4$.—When potassium chloride or nitrate is treated with excess of sulphuric acid until the hydrochloric or nitric acid is volatilized and the liquid is then allowed to cool, crystals of this salt separate out. Many minerals which withstand the action of acids, are brought into a soluble form by fusion with this salt.

There are other sulphates in which the proportion of the basic oxide is smaller than in the above cases. The principal of these are the *pyrosulphate*, $K_2S_2O_7$, or $K_2O.2\ SO_3$, the *tetrasulphate*, $K_2S_4O_{13}$, or $K_2O.4\ SO_3$, the *octosulphate*, $K_2S_8O_{25}$, or $K_2O.8\ SO_3$. They are obtained by the action of excess of sulphuric acid or fuming sulphuric acid on the normal sulphate, and occur with potassium, cæsium, and rubidium, but have not been prepared in the case of sodium, lithium, or the alkaline earths.

Potassium persulphate, $K_2S_2O_8$, must be regarded as a derivative of the liquid oxide S_2O_7, which has been isolated by Berthelot. The salt is obtained on electrolyzing an acid solution of potassium sulphate; it is sparingly soluble in cold water; in presence of water it is slowly decomposed into potassium hydrogen sulphate, and oxygen.

Potassium nitrate, KNO_3, known also by the familiar names *nitre* or *saltpetre*, is found in the surface soils in India, Persia, where a sufficiency of nitrogenous matter exists, and the climate is sufficiently dry to allow of its accumulation. It is also prepared by boiling together concentrated solutions of Chili saltpetre ($NaNO_3$) and potassium chloride, when a double decomposition takes place, and the less soluble sodium chloride separates out; potassium nitrate is crystallized out from the mother liquor. It is obtained also artificially by a method resembling that by which it is formed in the soils of eastern countries. Heaps of ashes are drenched with urine and other nitrogenous refuse; after being exposed to the air for some time the nitrogenous substances become oxidized, and, on lixiviation, the liquor is found to contain large quantities of nitrates. Treatment with potassium carbonate gives rise to the formation of potassium nitrate, which can be extracted in a crude form by crystallization.

Potassium nitrate is very soluble in water; 100 parts of water at 15° C. dissolve 26 parts of salt, and at 100° C. about 250 parts.

When strongly heated, it gives off oxygen, and is transformed into potassium nitrite, KNO_2, and in presence of charcoal a violent deflagration takes place, the reaction which takes place approximating to the equation—

$$4\,KNO_3 + 5\,C = 2\,K_2CO_3 + 3\,CO_2 + 2\,N_2.$$

Potassium nitrate is therefore a powerful oxidizing agent, organic substances and carbonaceous matter being readily decomposed with the formation of potassium carbonate, carbon dioxide and carbon monoxide when they are fused with it.

Sulphur under similar circumstances is oxidized with the formation of potassium sulphate and sulphur dioxide—

$$2\,KNO_3 + 2\,S = K_2SO_4 + SO_2 + N_2.$$

Gunpowder.—A mixture of potassium nitrate, charcoal, and sulphur finds application as gunpowder, the propelling power of which is due to the fact that the nitrate supplies oxygen by which the combustion of the sulphur and carbon is effected in a closed space. The volume of the gases generated, even when measured at the standard temperature and pressure, amounts to about 380 times that of the space occupied by the gunpowder; as the temperature generated is over 2000° C., it is evident that the volume is very much greater, and the pressure to which they give rise has been estimated at over 6000 atmospheres, or about 42 tons on the square inch. The composition of gunpowder varies according to the use to which it is to be applied; typically it has the proportions agreeing with the formula $2\,KNO_3 + 3\,C + S$, and the percentage composition of some forms of it is given in the following table;—

		KNO_3	C.	S.
$2\ KNO_3 + 3\ C + 1\ S$	=	74·8	13·4	11·8
English military powder	=	75·0	15·0	10·0
„ sporting „	=	79·7	12·5	7·8
Ordnance „	=	73·8	13·4	12·8

Phosphates and arsenates of potassium.—The ortho-salts are in general obtained by the addition of potash or potassium carbonate to solutions of the respective acids. The acids possess three atoms of hydrogen, which may be replaced atom by atom according to the relative quantity of potash added, thus—

$$H_3PO_4 + KOH = KH_2PO_4 + H_2O$$
$$\text{„} + 2\ KOH = K_2HPO_4 + 2\ H_2O$$
$$\text{„} + 3\ KOH = K_3PO_4 + 3\ H_2O$$

and similarly with the arsenates.

The *pyrophosphate* $K_4P_2O_7$ is obtained by igniting the di-potassium salt, K_2HPO_4, and the *metaphosphate*, KPO_3, by igniting the mono-potassium salt, KH_2PO_4, thus—

$$2\ K_2HPO_4 \text{ by ignition } = K_4P_2O_7 + H_2O$$
$$KH_2PO_4 \quad \text{„} \quad = KPO_3 + H_2O$$

Potassium carbonate, K_2CO_3, has been mentioned already as occurring in the incinerated residue from plants. It is also prepared from the sulphate by a method corresponding to the Leblanc process, by which sodium carbonate is obtained. (See page 145.) By the action of carbon dioxide, the bicarbonate, $KHCO_3$, is obtained. Both salts are freely soluble in water, the former, at ordinary temperatures, in its own weight of water, and the latter in four times its weight of water. Potassium carbonate withstands high temperatures without decomposition, but the bicarbonate readily loses carbon dioxide and water, and is transformed into the carbonate—

$$2\ KHCO_3 = K_2CO_3 + CO_2 + H_2O.$$

Like several other of the salts of potassium derived from weak acids, the normal salt possesses an alkaline reaction.

Borate and silicate of potassium.—These salts are prepared by heating together boric acid or silica respectively with potassium carbonate, the former having the composition KBO_2, and the latter K_2SiO_3.

Detection and estimation.—Potassium is characterized—

(1) By giving a white precipitate of cream of tartar, $KH_5C_4O_6$, when tartaric acid is added to a fairly concentrated solution of its salts.

(2) By the yellow precipitate (K_2PtCl_6) on the addition of platinic chloride, $PtCl_4$; ammonium, rubidium, and cæsium salts are likewise precipitated by the same reagent, the double chlorides of sodium and lithium being, however, readily soluble.

(3) By the violet colour imparted to the non-luminous flame of a Bunsen burner, the spectroscope showing a prominent line in the red (the A line), and one in the violet (near the H line).

Potassium is usually estimated in the form of the double salt with platinic chloride K_2PtCl_6, which, though somewhat soluble in water, is practically insoluble in alcohol.

AMMONIUM

This name is applied to the hypothetical radical NH_4, the salts of this radical being very similar in general character to those of the alkalies. When sodium amalgam is brought into a strong solution of ammonium chloride it swells up to many times its original bulk and forms a spongy mass owing to the inclusion of a large volume of gas. No sooner is this brought about than ammonia and hydrogen are given off from the mass in such proportions as to point to NH_4 as the source thereof. It has, however, never been established that the NH_4 exists even temporarily in the free state.

Ammonium salts are invariably obtained by the combination of ammonia with the acid of the salt; thus, neutralizing various acids with ammonia, we have—

$$2\,NH_3 + H_2SO_4 = \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4}$$

$$NH_3 + HCl = \underset{\text{Ammonium chloride.}}{NH_4Cl}$$

$$NH_3 + HNO_3 = \underset{\text{Ammonium nitrate.}}{NH_4NO_3.}$$

Coal contains between 1 and 2 per cent. of nitrogen, and during its distillation for the production of coal gas some of this is transformed into ammonia, and on washing the coal gas it is dissolved out. Gas liquor consists of these washings and contains considerable quantities of ammonia, mostly as sulphide, but partly in other forms and as free ammonia. By distilling the liquor over lime the ammonia is set free and then "fixed" by passing it into sulphuric (or sometimes hydrochloric) acid. The ammonium salts which come into commerce are chiefly obtained from gas liquor, the bulk of the supply being used in the form of ammonium sulphate as a fertilizing agent, and a considerable amount as free or caustic ammonia in the ammonia soda process.

Ammonium fluoride, NH_4F, is prepared by saturating hydrofluoric acid with ammonia. It is employed in the laboratory as a means of decomposing insoluble silicates, the silica being volatilized as silicon tetrafluoride—

$$SiO_2 + 4\,NH_4F = SiF_4 + 4\,NH_3 + 2\,H_2O.$$

Ammonium chloride, NH_4Cl, is obtained as above or by direct combination of ammonia and hydrochloric acid in the gaseous condition. If ammonium chloride be heated, it sublimes, and this method is employed for its purification; when heated with exposure to air it is partially decomposed, and free ammonia and hydrochloric acid may be detected in the products. It is used in dyeing and in soldering and tinning, also as a reagent in the laboratory. It crystallizes in the regular system and is freely soluble in water and in alcohol.

Ammonium sulphate, $(NH_4)_2SO_4$, is obtained as described above; the *octosulphate* $(NH_4)_2S_8O_{25}$ and the *persulphate* $(NH_4)_2S_2O_8$ are also known, and may be prepared by the same methods as are adopted in the case of the corresponding potassium salts.

Ammonium nitrate, NH_4NO_3, is prepared by neutralizing nitric acid with ammonia and evaporating the solution until it crystallizes on cooling. When heated it breaks up into nitrous oxide and water. $NH_4NO_3 = N_2O + 2\,H_2O$. When rapidly heated as for instance by contact with a red-hot metal, it detonates, as it does also when heated in presence of organic matter, and it is used in the production of certain forms of explosives.

By the direct combination of ammonia and carbon dioxide in presence of moisture, or by subliming an intimate mixture of ammonium sulphate and chalk, there is obtained the commercial carbonate of ammonium, which is however essentially a mixture of *bicarbonate* NH_4HCO_3 and *carbamate* $CO\left\{\begin{matrix}NH_4O.\\NH_2.\end{matrix}\right.$ These compounds are very unstable and undergo slow decomposition even at ordinary temperatures, and this accounts for the ammoniacal odour which is perceived when they are exposed to air.

Detection and estimation.—

(1) When heated with caustic alkalies the whole of the ammonia is given off, and may be detected by its smell and by yielding white fumes in presence of hydrochloric acid.

(2) Ammonium salts, like potassium, when treated with platinic chloride give rise to the formation of a yellow precipitate owing to the formation of the double chloride $(NH_4)_2PtCl_6$.

(3) Nessler's reagent (see p. 178), in presence of minute quantities of ammonia or ammonium salts, gives a yellowish brown colouration, or if larger quantities are present, a brown precipitate.

Ammonium salts may be separated from other alkalies by reason of their volatility. They may be estimated by distilling with caustic soda and passing the ammonia so formed into dilute hydrochloric acid of known strength, and then ascertaining to what extent the diminution in acidity of the acid has been effected. Or the ammonium chloride so formed may be precipitated by the addition of platinic chloride. By igniting the double chloride, spongy platinum only is left, whilst with other alkalies a mixture of spongy platinum and the alkaline chloride remains.

SODIUM.

Occurrence.—

(1) As common salt, in sea water, and some inland lakes, and in lenticular deposits in rocks, more especially in the strata of the age of the new red sandstone.

(2) As nitrate (Chili saltpetre) in the west of South America.
(3) Occasionally in springs or inland lakes as sulphate, carbonate or borate.
(4) In many mineral silicates.

The two first sources afford the principal supply of the raw material for the production of sodium salts.

Metal.—The methods employed for the preparation of metallic sodium are similar to those already described for potassium. Recently, the process of electrolyzing fused caustic soda has been so far perfected as to afford a most ready means of isolating sodium. This method has been mentioned under potassium, but we shall add here some details of the plant by which it is carried into practice.

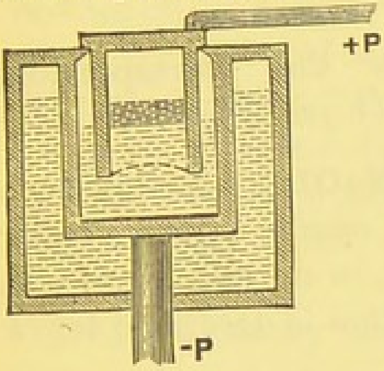


FIG. 23.

It consists essentially of a cylindrical iron pot containing the fused caustic soda, and surrounded by a bath heated by gas. Passing in at the base of the pot, as shown in Fig. 23, is the electrode in connection with the negative pole of the dynamo; the positive pole of the dynamo is connected with the cover of the pot, and with an inverted iron cylinder attached to the cover. The annular space between the electrode is that through which the current passes, and in which the decomposition goes on.

Hydrogen and sodium are formed at the negative electrode, and the former is allowed to pass out by a perforation in the cover, whilst the sodium being lighter than the fused caustic soda rises to the surface immediately above the electrode. A second inverted cylinder attached to the cover, and of a somewhat larger diameter than the negative electrode, serves as a receptacle for the sodium. In this the sodium collects, and it is removed from time to time by means of a ladle, perforated so as to allow any caustic soda to run back into the vessel.

The success of the operation depends upon a careful adjustment of the current, and on maintaining the caustic soda at such a temperature that it is always a few degrees above its melting point.

Sodium is a soft malleable metal of specific gravity 0·974; it shows a silvery lustre when freshly cut, but rapidly tarnishes through oxidation, even at ordinary temperatures. It melts at 92° C., and is transformed into a violet vapour at about 740° C. It burns vividly in oxygen and in chlorine, though these gases have no action upon it when perfectly dry. Like potassium it decomposes water at the ordinary temperature, the heat generated in the reaction being insufficient to ignite the hydrogen (as it does in the case of potassium); if the sodium be, however, brought into contact with hot water, or water thickened with starch, the hydrogen inflames.

Sodium hydride, Na_4H_2, resembles the corresponding hydride of potassium in its formation and properties.

The hydroxide or caustic soda, NaOH.—Caustic soda is prepared on a much larger scale than caustic potash, being used in the manufacture of soap and paper, in the refining of oils, and for many other purposes. Its production is described below (p. 148).

It may also be obtained by other methods described under caustic potash, which it resembles in its properties, though it is less deliquescent, and is not so strong a base as this body.

The Oxides.—When sodium is heated in air or oxygen it is almost completely transformed into the *dioxide* Na_2O_2. This oxide is a white amorphous powder which dissolves in water without decomposition, and from such a solution, crystals having the composition $Na_2O_2 8\ H_2O$ may be obtained. In presence of dilute acids it yields hydrogen peroxide

$$Na_2O_2 + 2\ H_2SO_4 = 2\ NaHSO_4 + H_2O_2.$$

It is made on a moderately large scale for the preparation of hydrogen peroxide now employed either directly or indirectly (as with magnesia) for bleaching purposes.

The chemistry of the *sulphides* and *nitride* of sodium will be understood by reference to the corresponding potassium compounds, which they resemble.

In like manner the description of the haloid salts of potassium may *mutatis mutandis* be taken as bearing upon the derivatives of sodium and the remarks added below regarded as supplementary thereto.

Sodium chloride or common salt, $NaCl$.—This is by far the most important material as a source of sodium salts. In some cases it is obtained in the solid state from mines, but more usually it is brought to the surface in the form of brine and the salt recovered from this by evaporation in pans. On the Continent, in the case of weak brines it is customary to subject the liquor to a preliminary concentration by allowing it to pass over stacks of twigs or brushwood. In England, much of the salt is raised as brine, and some idea may be formed of the extensive use which is made of it, from the fact that over two million tons of salt are produced annually, three-fourths of this in Cheshire, and the rest chiefly in Worcestershire and Durham. Common salt is used as a glaze for earthenware and for culinary purposes, also as the means of producing "salt-cake" (sodium sulphate), washing soda and "soda ash" (sodium carbonate) and caustic soda, etc.

Under ordinary circumstances it separates out on evaporation in the anhydrous condition, but at $-10°$ C. it is obtained as $NaCl2H_2O$ and at $-23°$ C. as $NaCl10H_2O$. It is practically insoluble in concentrated hydrochloric acid and in alcohol and by saturating a strong brine with hydrochloric acid gas it is deposited in a state of great purity.

Sodium chlorate, $NaClO_3$.—This salt is very much more soluble in water than potassium chlorate, and hence is more suitable for use in cases where chlorates are employed in solution. It may be prepared from calcium chlorate liquors from which most of the chloride has been previously removed by crystallization, by the addition of sodium sulphate in such a way that the change effected is that represented by the equation—

$$Ca(ClO_3)_2 + Na_2SO_4 = 2\ NaClO_3 + CaSO_4.$$

The sulphate of lime is filtered off and the liquor, which also contains sodium chloride, is concentrated; the sodium chloride separates out, and when sufficiently concentrated the mother liquor is cooled, whereupon the sodium chlorate is obtained in crystals.

Sodium hydrogen sulphite, $NaHSO_3$, is prepared in solution by passing sulphur dioxide to saturation into caustic soda or sodium carbonate (CO_2 being in this case expelled). By cooling or evaporation *at ordinary temperature* the salt is obtained in crystals. If exposed to air it becomes slowly oxidized to sodium sulphate; it also absorbs chlorine and may therefore be used for removing the last traces of chlorine from paper pulp. It dissolves sulphur, forming sodium thiosulphate, $Na_2S_2O_3$ (which is likewise used as an antichlor), also the haloid salts of silver. If a quantity of soda equal to that originally used in preparing the salt be added, neutral *sodium sulphite,* Na_2SO_3 is obtained. Both these salts are powerful reducing agents owing to the facility with which they pass into sodium sulphate.

Sodium sulphate or salt-cake, Na_2SO_4.—This salt is also known by the name of Glauber's salts, Glauber having described it as early as 1658. Most of the common salt raised in England is converted first into salt-cake by the action of sulphuric acid. This is done in two stages, the first being carried out at a gentle heat in a shallow cast-iron pan (see Fig. 24), the reaction being—

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

The charge is then raked out of the pan and exposed to a stronger heat on the bed of a reverberatory furnace, when further action takes place as expressed in the following equation—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

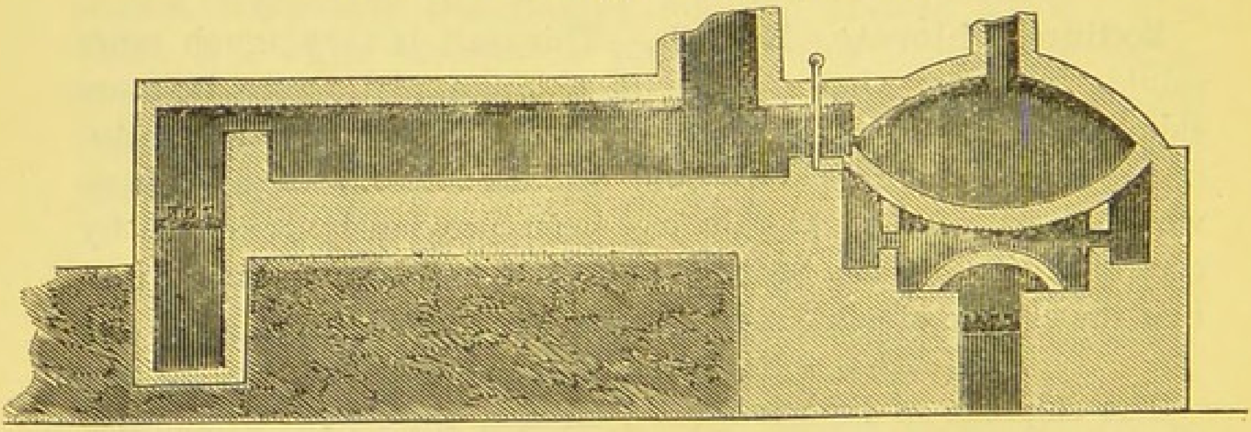


FIG. 24.

It would thus appear that half the hydrochloric acid is given off during the treatment in the pan (called "pan-gas") and half during roasting on the bed of the furnace (called "roaster gas"), though these equations do not accurately represent the stages as they occur in practice, for a larger proportion of the gas is evolved in the former process. The hydrochloric acid gas is cooled and condensed by being passed first through a series of pipes and ultimately through towers packed with coke over which a continual stream of water is kept flowing.

Sodium sulphate in a very pure form is also prepared by the Hargreaves process. This consists in bringing sulphur dioxide (prepared from iron pyrites), air and steam into intimate contact with common salt at about 500° C. The reaction which ensues may be represented by the equation—

$$4\,NaCl + 2\,SO_2 + O_2 + 2\,H_2O = 2\,Na_2SO_4 + 4\,HCl.$$

Sodium nitrate or Chili saltpetre, $NaNO_3$, is found in the almost rainless districts of Chili, Peru and Bolivia. It is very soluble in water, from which it crystallizes as the anhydrous salt in obtuse rhombohedra almost like cubes (hence the name "cubic nitre"). It is largely used as a manure and also in the manufacture of sulphuric acid and nitric acid. It cannot be substituted for potassium nitrate in gunpowder owing to its hygroscopic nature.

Phosphates and arsenates of sodium are similar in character to the corresponding potassium salts.

Sodium carbonate, Na_2CO_3, was formerly obtained by burning seaweed and extracting the ash with water. In this crude form it was known as *barilla*.

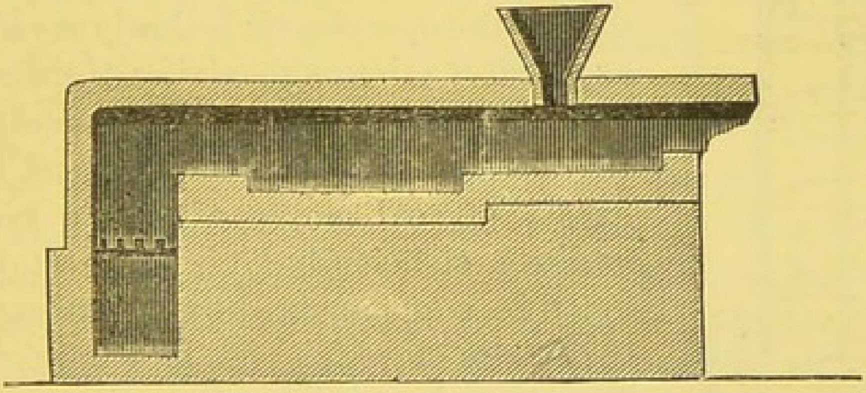


FIG. 25.

It is now prepared from common salt either directly or after the conversion into salt-cake by processes which we shall now describe, the former as the Solvay process, and the latter as the Leblanc process.

The Leblanc process.—A charge usually of about four hundredweight of a mixture of salt-cake with its own weight of coal is brought on to the upper bed of the furnace shown in Fig. 25, where it is gently heated and worked so as to incorporate the constituents together. It is then exposed to the higher temperature of the lower bed and thoroughly mixed, the operation being continued until "candles" of carbon monoxide break out over the surface of the mass. The primary reaction is—

$$Na_2SO_4 + CaCO_3 + 2\,C = Na_2CO_3 + CaS + 2\,CO_2.$$

Towards the end, carbon monoxide is given off owing to the interaction between the excess of limestone and coal used—

$$CaCO_3 + C = CaO + 2\,CO.$$

The "ball" is now drawn and constitutes what is known from its colour as "black ash." It is allowed to cool for some hours and is then roughly broken up and thrown into vats, where the sodium carbonate is dissolved out to form "tank liquor," and a bulky residue called "tank waste" or alkali waste (see page 155) is left.

It is now more usual to dispense with the hand-working by carrying on the process in a "revolver" furnace. This is practically a large drum lined with fire-brick; during the operation it is slowly revolved so as to effect a thorough mixing of the charge. Heat is generated within the revolver by the reaction which takes place and by the excess of coal employed, but in order to secure a sufficiently high temperature this must be supplemented by an external fire, the flames of which pass into the revolver. The waste heat arising from either of these processes is very considerable, and it is utilized for the purpose of boiling down the liquor obtained on lixiviating the black ash.

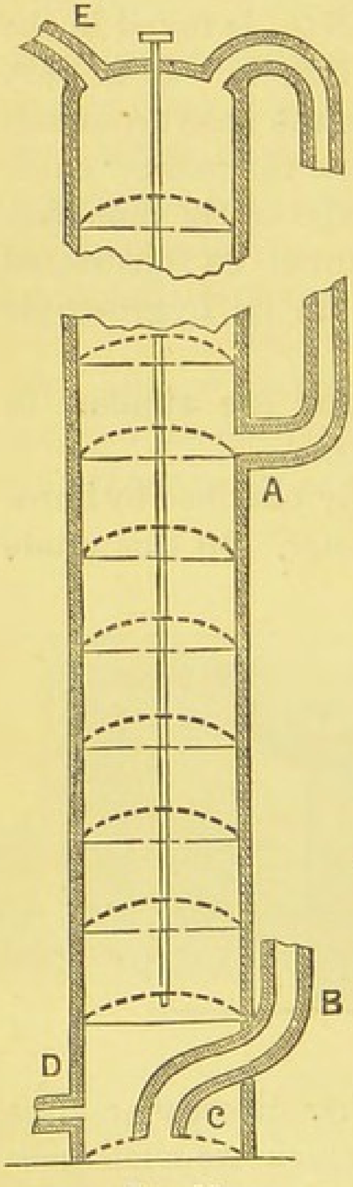


FIG. 26.

The liquor is run into shallow pans and the waste gases passing over its surface bring about a concentration to such an extent that the crude sodium carbonate separates out. The salts are drawn on to drainers placed at the front of the pans. In this way the impure monohydrated carbonate, $Na_2CO_3.H_2O$, is obtained, whilst any caustic soda and most of the other impurities remain in the mother liquor. This is now calcined in a reverberatory furnace to get rid of the water of crystallization and also to burn off organic matter and transform as much as possible of the impurities (such as sulphide and hydrate) into carbonate, known in commerce as *soda ash*.

The ammonia soda process.—By this process common salt is converted *directly* into sodium bicarbonate. It consists essentially in passing carbon dioxide through an ammoniacal solution of common salt, when the reaction takes the form—

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$

Brine is first almost saturated with ammonia and is then run through the pipe A down a tower built of sheet-iron of the construction shown (Fig. 26). The tower is 6ft. in diameter and at least 50ft. high; at intervals of about 3ft. there are compound diaphragms made up of a horizontal flat plate with a large hole in the centre, and over this a curved plate perforated with small holes and deeply cut into grooves round the circumference, as shown in Figs. 27 and 28. The carbon dioxide is forced in under pressure at the base of the tower at B, and as it rises upwards it meets at the perforations the thin layer of brine which spreads itself over the sieve-like plates. The sodium bicarbonate which forms is carried down through the slits at the edge of the diaphragm. It collects at the base of the tower C, forming a fluid of creamy consistency, and this is periodically

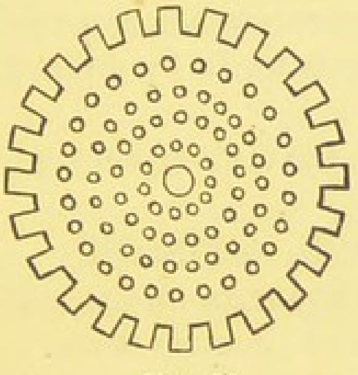


FIG. 27.

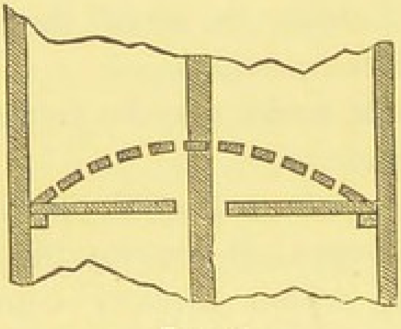


FIG. 28.

drawn off at D, and the salt is separated from it by filtration. The carbon dioxide carries forward with it a certain amount of ammonia which is recovered by washing the gas after it leaves the upper part of the tower by the pipe E; in order to reduce the quantity of ammonia carried off in this way it is usual to introduce the brine at about the middle of the tower. The bicarbonate is heated in order to transform it into carbonate—

$$2\ NaHCO_3 = Na_2CO_3 + H_2O + CO_2,$$

and the carbon dioxide used in the process is obtained partly in this way but chiefly (mixed with nitrogen) from lime-kilns.

It will be noticed that ammonium chloride (also ammonium carbonate) is formed and remains in the liquors. The ammonia alone is recovered from this by heating it along with milk of lime in a specially constructed still—

$$2\ NH_4Cl + CaO = CaCl_2 + 2\ NH_3 + H_2O.$$

$$(NH_4)_2CO_3 + CaO = CaCO_3 + 2\ NH_3 + H_2O.$$

The whole of the chlorine contained in the sodium chloride is lost and passes away in the waste liquors as calcium chloride, but this loss is compensated by the purity of the resulting sodium carbonate, and by the economy in this process as compared with that of Leblanc, in which the carbonate is made by a much more complicated method.

Caustic soda may be prepared from the tank liquor by boiling it with lime—

$$CaO + Na_2CO_3 + H_2O = CaCO_3 + 2\ NaOH,$$

but it is usual to employ the mother liquor from the pans and drainers, which already contains much caustic soda. Such liquors contain considerable quantities of sulphide, thiosulphate, cyanide and some sulphate of sodium, and before being treated with lime they are oxidized either by blowing air through the hot liquor or by the addition of nitre. The boiling with lime and the earlier stages of the concentration of the caustic liquor are done in large open pans, termed from their shape "boat-pans." It is then settled and the clear liquor finally boiled down in large hemispherical pots called "finishing pots." As the water is gradually evaporated off in these pots the temperature of the mass rises from 140° C. until it reaches 260° C.; towards the end of this process, owing to the high temperature, the cyanides are decomposed and a scum of graphite forms at the surface. Finally a further oxidation is performed by blowing or by the addition of nitre, and the temperature is maintained for some hours whilst oxide of iron and other impurities settle out, and the fused caustic soda is then run into iron drums where it solidifies.

Silicates of sodium.—A strong solution of sodium silicate, known as water-glass, is used for coating the surface of stone; it is also employed in the manufacture of certain forms of soap, in calico printing, wool cleansing, etc. It is prepared by fusing sodium carbonate with sand or by heating sand with caustic soda under pressure.

Sodium biborate, borax, $Na_2B_4O_7 10H_2O$, occurs as a deposit on the site of dried-up inland lakes in some parts of India, in Tibet, and in California. It is extracted by simply boiling with water until a concentrated solution is obtained, and then after settling it is allowed to crystallize out. The boric acid from the lagoons of Tuscany also furnishes it by digestion with soda-ash. It crystallizes in monoclinic prisms and is very much more soluble in hot water than cold; 100 parts of water dissolve about five parts of borax at ordinary temperatures and about 200 parts at 100° C. When heated, it is transformed into a soft spongy mass consisting of the anhydrous salt which is used in welding iron. Borax finds many applications in the arts, and being a powerful antiseptic it is employed for preserving articles of food.

Detection and estimation.—The sodium salts are almost all freely soluble in water, but from moderately strong solutions they are precipitated by the addition of potassium metantimoniate, $KSbO_3$. (See p. 253.) The presence of sodium, even in very small quantities, may be recognized by the bright yellow colour given to the flame. In the spectroscope a yellow line coinciding with the Fraunhofer line D is seen, which under sufficient dispersion proves to be double.

Sodium is usually estimated in the form of sulphate, obtained by heating with excess of sulphuric acid to dull redness.

CHAPTER IX.

THE ALKALINE EARTHS,

Ca, Sr, Ba.

General Characters.—

1. As in the case of the alkalies, the metals are obtained by electrolysis of the fused chlorides, and the resemblance extends to the character of the metals, which are (*a*) soft and malleable, (*b*) decompose water at ordinary temperatures, (*c*) become oxidized without the application of heat when exposed to air or oxygen.
2. They are dyads, and replace two atoms of hydrogen in the acids, and thus their compounds are represented by the typical formulæ RCl_2, RSO_4, RCO_3, etc.
3. The oxides dissolve in water, forming strongly basic hydroxides, which however are less caustic and less soluble than those of the alkalies. The solubility *increases* in the order Ca, Sr, Ba, that is as the atomic weight rises.
4. They form dioxides (peroxides); but only in the case of barium is the dioxide formed in the dry way, that is, by heating the oxide in air.
5. The haloid salts (except the fluorides) and nitrates are readily soluble in water, and the fluorides, sulphates, phosphates and carbonates either insoluble or only slightly soluble, the solubility *decreasing* in the order Ca, Sr, Ba, *i.e.* with rising atomic weight.
6. The carbonates are decomposed at a red heat.

7. They form carbides of the composition RC_2, and these re-act with water at ordinary temperatures, producing hydrocarbons, mainly acetylene.

CALCIUM.

Occurrence.—As *carbonate* (limestone) it is found in rock masses, and also in crystals as calcite and aragonite; as *sulphate* in the forms anhydrite, the anhydrous sulphate, $CaSO_4$, and gypsum, or selenite (hydrated), $CaSO_4.2H_2O$, as *fluoride* in fluorspar, CaF_2, and as *phosphate* in apatite, Ca_32PO_4. Dolomite (and magnesian limestone) is calcium carbonate in which part of the calcium is replaced by magnesium, $CaMgCO_3$.

Metal.—Obtained by heating the anhydrous iodide with sodium, or by electrolyzing the fused chloride, preferably mixed with strontium or barium chloride, in order that the fusion may be brought about at a lower temperature. It is, like the other metals of this group, a soft, malleable metal, having a bright surface when freshly cut, and like them also it readily decomposes water at ordinary temperature.

Oxides and hydroxides.—The *monoxide*, CaO, is usually obtained by igniting limestone, mixed with coal, in a kiln. It is termed "quicklime," and when brought into contact with water combination takes place, and a considerable amount of heat is evolved, calcium hydroxide, $Ca(OH)_2$, being formed. The lumps of lime fall to powder when thus treated, "slaked" lime being produced; with sufficient water to bring it to a creamy consistency, "milk of lime" is produced.

Calcium oxide, or lime, is infusible even in the oxy-hydrogen blowpipe. It dissolves at ordinary temperatures in about 700 parts of water; the limewater so formed has an alkaline reaction, readily absorbs carbon dioxide, and becomes transformed into the carbonate.

The *dioxide*, CaO_2, is prepared by adding hydrogen peroxide to limewater. In the dry way (by heating the pure carbonate) it is only formed in small quantity.

Ordinary mortar is made by mixing lime in the moist state with three or four times its weight of sand. The hardening of mortar is due to its gradual transformation into carbonate, and to some extent silicate; and it has been found that the setting of mortar takes place more rapidly when carbonaceous matter, or ammonium carbonate, is brought into intimate admixture with it. Certain siliceous limestones, when burnt, form hydraulic mortar or cement which possesses the property of hardening under water. Portland cement, for instance, contains over 20 per cent. of silica as well as about 10 per cent. of the oxides of alumina and iron.

Lime-burning.—Lime, CaO (known technically as *quicklime*), is obtained on the large scale by the action of heat on limestone, $CaCO_3$.

The decomposition of limestone and the conditions favourable to it will be understood by reference to pages 27 and 28. From a consideration of these conditions it appears that to secure a complete transformation of the limestone into lime, it is necessary to sweep out the carbon dioxide gas which is liberated.

For successful lime burning it is therefore essential to heat up the mass to bright redness (the temperature should not much exceed 1000°C), and to provide such a form of kiln as shall furnish a draught of air sufficient to displace the carbon dioxide so soon as it is set free. The presence of a certain amount of moisture is advantageous, since it is found that steam facilitates the operation.

The fuel used should burn with little ash, and may consist of wood, coke, or coal. Two forms of kilns are still in use, the older form is usually egg-shaped and has a fire grate at the bottom, a layer of large pieces of limestone is arranged over this in the form of an arch, and above this smaller pieces are placed until the kiln is filled up to the top. A fire is lighted under the arch of limestone and kept burning for three days and nights, by which time the whole of the limestone is converted into quicklime and can be raked out at the bottom. In the more modern or continuous process the kilns are bucket shaped, or similar in form to an ordinary blast furnace (see Fig. 35), and often as much as 30 ft. high. In these the fuel and limestone are charged in alternating layers in the proportion of about one part of fuel to four parts of limestone, and at the base of the kiln are gratings and dampers for admitting and regulating the supply of air. In some recent forms of kiln arrangements have been made for using producer-gas as the source of heat, the operation being under these circumstances much more easily controlled than where solid fuel is used.

The quality of the quicklime varies according to the nature of the limestone from which it is made. Quicklime which slakes readily giving out much heat is called *fat lime*, whilst the kind which contains much silica, alumina, and magnesia, and which slakes feebly is called *poor lime.*

Sulphides of calcium.—The *monosulphide*, CaS, is obtained by heating together a mixture of the sulphate with coal; as prepared in this way it is a white powder, soluble to some extent in water, forming the hydrosulphide $Ca(SH)_2$. It possesses the property of appearing luminous in the dark after it has been exposed to sunlight, the sulphides of strontium and barium likewise exhibiting this character. Phosphorescence is also shown by apatite, and by green fluorspar when heated. By digesting flowers of sulphur with milk of lime, other sulphides, varying in composition between the *disulphide* CaS_2, to the *pentasulphide* CaS_5. may be obtained.

All these bodies readily decompose in presence of acid, giving off H_2S, and in the case of the higher sulphides depositing sulphur; by the addition of concentrated hydrochloric acid in large excess to the higher sulphides, the liquid H_2S_2 separates out. The tank waste remaining after lixiviation of black ash contains such sulphides, or more probably an oxysulphide of the composition $2\,CaS.CaO$.

Recovery of sulphur from tank waste.—Many processes have been suggested for recovering sulphur from these residues. Two of the most interesting which have been adopted to the greatest extent are the Mond process and the Chance-Claus process.

The Mond process.—This consists essentially of weathering or oxidizing the waste until *part* of the sulphide is oxidized to thiosulphate, CaS_2O_3, and treating the residue with hydrochloric acid:—

$$CaS_2O_3 + 2\,HCl = CaCl_2 + S + SO_2 + H_2O$$
$$\text{(unchanged) } 2\,CaS + 4\,HCl = 2\,CaCl_2 + 2\,H_2S.$$

If the oxidation has been allowed to proceed only so far as to transform one-third of the sulphide into thiosulphate, the proportion of the H_2S to that of the SO_2 produced will be 2 : 1, as shown in the equations. Then by the interaction of the H_2S and SO_2 mutual decomposition takes place, and the whole of the sulphur is set free—

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

The Chanoe-Claus process.—The tank waste is finely powdered and suspended in water; carbon dioxide is then forced through the liquid; the following reaction takes place:—

$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2\ H_2S$$

The H_2S is then burnt in closed kilns containing oxide of iron, with just sufficient air to effect the combustion of the hydrogen:

$$2\ H_2S + O_2 = 2\ H_2O + S$$

The sulphur, which separates, for the most part collects at the bottom of the kiln or in a brick chamber attached thereto in the molten condition, and is periodically run off.

Calcium Carbide, CaC_2.—This body is made on a moderately large scale by exposing a mixture of 3 parts of lime and 2 parts of coke in a closed furnace to the action of a powerful electric current by which a high temperature is generated. Strontia and baryta under similar circumstances form corresponding carbides. These carbides when treated with water furnish ready supplies of almost pure acetylene in large quantity, a pound of the carbide yielding about 5 cubic feet of the gas:—

$$CaC_2 + H_2O = CaO + C_2H_2.$$

Calcium fluoride, CaF_2, is found in cubical crystals or in masses, especially in districts where lead ores occur. It is either colourless or of a green or purple colour. It is used as a flux (whence its name) in many metallurgical operations, and serves to bring slags into a fluid condition at a lower temperature. It is insoluble in water and most acids, but concentrated sulphuric acid decomposes it, with the evolution of hydrofluoric acid, which is usually prepared in this way.

Calcium chloride, $CaCl_2$, is obtained as a waste product in the production of soda by the ammonia-soda process, in the recovery of manganese dioxide (see page 155), and in the manufacture of potassium chlorate. It is prepared on a small scale by acting on lime or calcium carbonate with hydrochloric acid. When exposed to air the anhydrous chloride readily deliquesces, and it is employed in the laboratory for drying gases. It is extremely soluble in water, and boiling saturated solutions deposit crystals of the, composition $CaCl_2.6\ H_2O$ on cooling. Like many other chlorides (*e. g.* of Ag, Hg, Cu) it takes up ammonia in a definite amount, forming $CaCl_2.8\ NH_3$.

Bleaching powder.—If chlorine be passed into milk of lime kept cool, calcium hypochlorite, $Ca(OCl)_2$ is formed—

$$2\ Ca(OH)_2 + Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O$$

in the hot milk of lime, calcium chlorate $Ca(ClO_3)_2$ is formed—

$$6\ Ca(OH)_2 + 6\ Cl_2 = 5\ CaCl_2 + Ca(ClO_3)_2 + 6\ H_2O.$$

If, however, *dry* slaked lime be exposed to an atmosphere of chlorine, it takes up about 37 per cent. of its weight of chlorine, and forms "bleaching powder," some of the lime remaining unaltered.

Manufacture of Chlorine and bleaching powder.—Chlorine is prepared on the large scale from the same materials (MnO_2 and HCl) as are employed in the laboratory. The vessel in which the reaction is carried on is usually a square or octagonal flagstone still holding a charge approaching half a ton of manganese dioxide and the requisite amount of hydrochloric acid. Heat is necessary, and as with such a still direct fire cannot be used, high pressure steam is blown in, especially towards the end of the operation.

The residue in the still at the end of the operation is still acid, and contains the manganese in solution as chloride ($MnCl_2$) ; this originally was run off to waste, but by the *Weldon recovery process* it is now possible to get most of the manganese back in the form of peroxide. The steps in the process are as follows :—

(1) The liquor is neutralised by adding to it powdered limestone or chalk, and iron salts, which are invariably present, undergo decomposition with the precipitation of ferric hydrate. This is allowed to settle out in tanks.

(2) To the settled clear liquor milk of lime in some excess is added, manganese is thrown down partly as manganous hydrate $Mn(OH)_2$ and partly in combination with lime.

(3) The precipitate is now warmed by steam, and oxidised by forcing air in small bubbles through the liquor. In this way calcium manganite $CaMn_2O_5$ (*i.e.*, a compound of lime and MnO_2) is formed it is known as "manganese mud."

The product so obtained has about 80 per cent. of the value for evolving chlorine of the original ore used, and when as much clear liquid as possible has been run off from it (after settling), this mud is run into the still and used over again. In so finely divided a condition the action would be too violent, and in order to check the rapidity of evolution of the chlorine it is usual to charge the requisite amount of hydrochloric acid into the still first and then run in the manganese mud gradually.

The "Deacon" process for the production of chlorine.—A mixture of hydrochloric acid gas and air (in the proportion of 4 volumes of air to one volume of hydrochloric acid gas) is heated up to 500°C and passed over broken bricks which have been caused to take up copper salts by being dipped into a solution of cupric chloride. At this temperature, and in contact with such materials, the oxygen of the air and the hydrochloric acid gas react so that a large percentage of the latter is decomposed and chlorine is liberated—

$$4\ HCl + O_2 = 2\ H_2O + 2\ Cl_2.$$

Even in the Weldon process the chlorine carries over with it moisture and hydrochloric acid gas from the stills, and before it is used in making bleaching powder it must be thoroughly cooled by passing through pipes in order that the acid and moisture may condense. In the Deacon process, however, much acid escapes decomposition, and such a method would be insufficient. In this case the hydrochloric acid gas must be washed out in coke towers and then dried by passing through strong sulphuric acid.

The production of bleaching powder.—The chlorine as obtained in the Weldon process is now passed into large chambers, about six feet high, on the floor of which dry slaked lime in fine powder is spread to the depth of 3 or 4 inches. The chlorine is gradually taken up by the lime, which is thus converted into bleaching powder capable of yielding 35 to 37 per cent. of chlorine on treatment with dilute acid.

The chlorine obtained by the Deacon process is weaker, *i.e.*, more diluted with air, and the chamber is divided up by horizontal shelves, and also partitioned vertically so as to expose a much larger surface to the chlorine, the slaked lime in this case being spread only to the depth of half-an-inch or a little over.

The constitution of bleaching powder.

Balard regarded it as $Ca(OCl)_2.CaCl_2$ together with $Ca(OH)_2$.
Stahlschmidt „ $Ca(OH)(OCl).CaCl_2.2\ H_2O$.
Odling „ $Ca(OCl)Cl$ and $Ca(OH)_2$.

It has been found that:—

(1) The *whole of the chlorine* may be expelled from it by exposure to moist carbon dioxide at 70° C.; it cannot therefore contain calcium chloride, since this is not decomposed by carbon dioxide. Moreover, it is not deliquescent ($CaCl_2$ is); and though calcium chloride is freely soluble in alcohol, an alcoholic extract of bleaching powder is only found to contain traces of chloride.

(2) The "available" chlorine, that is, the chlorine which is expelled by the action of dilute acids, amounts in samples which have been most carefully saturated, to 43½ per cent. and no more.

The formula of Odling alone completely satisfies these conditions, the percentage of available chlorine being such as to indicate the composition $2\ Ca(OCl)Cl.Ca(OH)_2$.

When bleaching powder is stirred up with cold water, the liquid shows an alkaline reaction owing partly to the solution of the hydroxide in the bleaching powder and partly to the formation of calcium hypochlorite, which possesses an alkaline reaction.

During decomposition either oxygen or chlorine may be set free according to circumstances. If dry bleaching powder be ignited or a concentrated extract be heated, oxygen is given off; by the action of dilute acids (even moist carbon dioxide) chlorine is liberated— $CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2$

$$CaOCl_2 + CO_2 = CaCO_3 + Cl_2.$$

In presence of certain oxides, *e.g.*, MnO_2, HgO, Fe_2O_3, CuO, CoO or its salts, oxygen is evolved, especially on warming. Sodium carbonate reacts with the formation of sodium chloride and hypochlorite and ammonia undergoes decomposition like that which it suffers in presence of chlorine, nitrogen being evolved.

$$CaOCl_2 + 2\ CoO = CaCl_2 + Co_2O_3$$

and then Co_2O_3 breaks up on warming into CoO and oxygen.

$$3\ CaOCl_2 + 2\ NH_3 = 3\ CaCl_2 + 3\ H_2O + N_2$$

$$CaOCl_2 + MnSO_4 + H_2O = CaSO_4 + MnO_2 + 2\ HCl.$$

Calcium sulphate, $CaSO_4$.—This body occurs in the mineral forms already mentioned, or may be precipitated by the addition of a soluble sulphate to a solution of a calcium salt. It possesses the singular property (lime resembles it in this respect) of being somewhat less soluble in hot water than cold, requiring over 500 parts of water to 100° C., but only 400 parts at 35° C. to dissolve it. When water containing calcium sulphate is used in boilers, a firm, coherent deposit of the salt gradually forms on the inner surface of the boiler. If rendered anhydrous by heating to about 140° C. it is converted into *plaster of Paris;* and this, made into a paste with water, gradually hardens, owing to its recombination with water. Calcium sulphate is very much more soluble in hydrochloric acid than in water.

Calcium orthophosphate, $Ca_3P_2O_8$.—This is the most important of the phosphates of lime; it occurs in bone and in mineral concretions known as "coprolites"; also, associated with chloride and fluoride respectively, as chlorapatite, $3\,Ca_3P_2O_8\,CaCl_2$, or fluorapatite, $3\,Ca_3P_2O_8.CaF_2$. The phosphate is only slightly soluble in water, though readily in acids, and is precipitated when a soluble phosphate, such as sodium phosphate, is added to the aqueous solution of a calcium salt in presence of ammonia. The "superphosphate of lime," used as a manure and for the preparation of phosphorus, is obtained by acting upon calcium phosphate (bone-ash) with sulphuric acid. It is a mixture of the acid calcium phosphate, $CaH_4P_2O_8$, with calcium sulphate.

Calcium carbonate, $CaCO_3$.—Mineral forms are Iceland spar or calcite, crystallizing in the hexagonal system, and aragonite crystallizing in rhombic prisms. Soluble calcium salts also yield a precipitate of the carbonate when treated with ammonium carbonate, and it is also obtained synthetically by the action of carbon dioxide on lime, or on lime water. It is practically insoluble in water, but soluble with the formation of the bicarbonate $CaH_2(CO_3)_2$ in excess of carbon dioxide, and in mineral acids, which latter, however, decompose it. It is found in many natural waters, being held in solution as $CaH_2(CO_3)_2$ by the excess of carbon dioxide, and as this escapes it becomes deposited as *tufa* or as *stalactites and stalagmites.*

Detection and estimation.—Calcium compounds that are volatilized in the non-luminous Bunsen flame impart to it a colour somewhat resembling that of strontium (and lithium), but duller and more of a yellow shade. The spectrum is a complex one, in which the orange double line of wave lengths, 6181, 6202, and a green line of wave length 5593 are prominent and characteristic.

The separation of the alkaline earths (Ca, Sr, Ba) from the alkalies is effected by means of the insolubility of their carbonates, which are precipitated on the addition of ammonium carbonate to a neutral or alkaline solution.

Calcium salts (except in very concentrated solution) are not precipitated by sulphuric acid, whilst strontium salts are slowly and incompletely precipitated, and barium salts are immediately and completely precipitated. This will be understood from the fact that $BaSO_4$ is soluble in 400,000 parts of water, $SrSO_4$ in 7000 parts, and $CaSO_4$ in 400 parts.

Calcium nitrate is readily soluble in alcohol, the corresponding salts of strontium and barium being insoluble; calcium nitrate may therefore be separated from the nitrate of strontium and barium by alcohol.

Calcium salts, in neutral or alkaline solution, are completely precipitated by ammonium oxalate, and by heating this in the blow-pipe flame till the weight becomes constant, CaO is left; by this method calcium is quantitatively estimated.

STRONTIUM.

Occurrence.—The minerals celestine, $SrSO_4$, and strontianite, $SrCO_3$, are the chief sources from which the strontium compounds are obtained. An isomorphous mixture of sulphates of barium and strontium, known as baryto-celestine, is also known.

The *metal*, the *oxides*, and *sulphides*, resemble those of calcium, the oxide, SrO, is, however, more soluble, 100 parts of water dissolving about 1·5 parts at ordinary temperatures, and 48 parts at 100° C. *Strontium hydroxide* is used for separating from molasses a quantity of cane sugar which cannot be crystallized out; it forms with the sugar a compound which is insoluble and readily separates. From this the sugar is obtained by suspending the compound in water and passing carbon dioxide, which transforms the strontia into carbonate, the sugar being left in the liquor.

The *chloride* and *nitrate* are readily soluble in water, but not to such a large extent as the corresponding calcium salts. They are obtained by the action of the respective acids on the oxide or carbonate. The nitrate is largely used in pyrotechny for red fire.

Detection and estimation.—Strontium salts give a pure crimson colour to the flame. In the spectroscope the characteristic and most intense lines are—the orange line (6059), the red lines (6694 and 6464), and the blue line (4607). The estimation is usually made as strontium sulphate, which, in presence of alcohol, is completely precipitated.

BARIUM.

Occurrence.—The minerals heavy spar or barytes, $BaSO_4$, and witherite, $BaCO_3$, and baryto-calcite, an isomorphous mixture of barium and calcium carbonate, are the most important forms in which barium is found. In small quantities it is widely distributed, and may be detected in some mineral waters and in sea water.

The *metal* is obtained by a similar method to that employed for calcium, which it resembles also in its properties.

The oxides and hydroxides.—By heating the carbonate or nitrate, the *monoxide*, BaO, is obtained, and this, when heated in air or oxygen, is gradually transformed into the *peroxide*, BaO_2. At a still higher temperature the oxygen thus taken up is again set free, and by alternately raising and lowering the temperature an unlimited amount of oxygen may be prepared in this way, using baryta as the intermediate body. The presence of moisture and carbon dioxide is detrimental, and after a few repetitions the baryta ceases to act efficiently; if, however, dry air freed from carbon dioxide is employed, the same charge of baryta may be used an unlimited number of times. This method of obtaining oxygen from the air has been worked on the large scale under the title of the Brin process. Instead of alternately raising and lowering the temperature, it is found more convenient to keep the temperature constant and vary the pressure. The furnace is kept at the temperature necessary to enable the baryta to take up oxygen and become converted into the peroxide; the pressure is then lowered to about $\frac{1}{10}$ of an atmosphere and the peroxide decomposes and gives up oxygen. The peroxide is soluble to some extent in water, and crystallizes therefrom as $BaO_2.8\ H_2O$. The peroxides of calcium and strontium are only obtained in the wet way by adding hydrogen peroxide to a solution of the hydroxide, but the peroxide of barium may be prepared by either this or the dry method just described.

Barium hydroxide, $Ba(OH)_2$, differs from the corresponding calcium and strontium compounds in being freely soluble in water, 100 parts of water dissolving about 3 parts of it at ordinary temperatures, and more than its own weight at 100° C. It readily absorbs carbon dioxide, forming barium carbonate, and from it the various salts of barium may be prepared by neutralizing with the corresponding acid.

It is worthy of remark that the poisonous character of the hydroxides and soluble salts of the alkaline earths increases with the atomic weight, calcium compounds being in general not markedly injurious to the system, and barium compounds highly poisonous, whilst strontium compounds are intermediate in respect of their toxic action.

Barium chloride, $BaCl_2$.—This salt is obtained by the action of hydrochloric acid on the oxide or carbonate (witherite). It is not deliquescent, being much less soluble than calcium chloride, and crystallizes with two molecules of water of crystallization, $BaCl_2.2\ H_2O$. The solubility of the chlorides of Ca, Sr, and Ba in 100 parts of water is as follows—

At	10° C.	40° C.	80° C.	100° C.
$CaCl_2$	60	110	142	155
$SrCl_2$	48	67	92	102
$BaCl_2$	33	41	52	59

It is almost insoluble in concentrated hydrochloric (or nitric) acid. It is used for preparing barium sulphate for use as the pigment known as *permanent white*, because it is unaffected by sulphuretted hydrogen or other impurities occurring in air; also for decomposing calcium sulphate in permanently hard water, and thereby preventing the incrustation which calcium sulphate forms.

$$CaSO_4 + BaCl_2 = BaSO_4 + CaCl_2.$$

The $BaSO_4$ being quite insoluble is precipitated in the form of a heavy white powder, which does not adhere to the boiler plates.

Barium chlorate, $Ba(ClO_3)_2$, is formed by adding barium carbonate to chloric acid. Barium chlorate is also obtained by passing chlorine into a hot solution of barium hydrate, just as calcium chlorate is, but the separation of the chloride in the liquor from the chlorate cannot be readily effected, because both these salts are approximately of the same degree of solubility. It is employed in pyrotechny, as is also the nitrate, for the production of green fire. When the salt is fused in an atmosphere of coal gas a vivid combustion takes place, the coal gas burning at the expense of the oxygen of the chlorate.

Barium sulphate, $BaSO_4$, is one of the most insoluble salts known. It may be obtained by direct union of the oxide with sulphur trioxide, the heat evolved during the combination being such as to raise the mass to incandescence. It is also formed whenever sulphuric acid or a soluble sulphate is added to a solution of a barium salt, and is the means by which sulphuric acid is quantitatively estimated. Though acids have, as a rule, no action upon it, hot concentrated sulphuric acid dissolves it somewhat readily, and the acid salt, $BaH_2(SO_4)_2$, separates on cooling, in crystals.

Barium nitrate, $Ba(NO_3)_2$, is obtained by dissolving the oxide or carbonate in nitric acid. An interesting method for its preparation consists in the mutual action of solutions of barium chloride and sodium nitrate, from which the less soluble sodium chloride separates out. Barium nitrate, like the chloride, is only slightly soluble in concentrated nitric acid, a white precipitate of the salt being formed when the acid is added in sufficient quantity to an aqueous solution of the salt. It is a powerful oxidizing agent, and when heated in presence of carbon it is decomposed with explosive violence.

Detection and estimation.—Those barium salts which are volatile at the temperature of the flame of a Bunsen burner, give rise to a characteristic apple-green colour. The principal lines in the spectrum are the green line (w.l. 5536), the yellow line (w.l. 5881), and, less strong, the orange line (w.l. 6044). The spectrum is a very complex one, and consists chiefly of a number of broad fluted bands.

Barium salts may be distinguished by being precipitated *at once* by a solution of calcium sulphate. When present in the form of acetate, barium, unlike calcium and strontium, is precipitated as chromate on the addition of potassium chromate, and in this way barium salts may be separated from the other salts of the alkaline earths.

It is invariably estimated in the form of barium sulphate.

CHAPTER X.

THE MAGNESIUM GROUP.

Mg, Zn, Cd, Hg.

General characters.—

1. The metals are more readily obtained than in the previous groups, being generally prepared by reduction of the oxides in contact with carbon. The reduction proceeds more easily the higher the atomic weight, the oxide in the case of mercury being decomposed by heat alone.

2. The molecule in the state of vapour consists of one atom, at any rate so far as Zn Cd and Hg are concerned. The melting points and boiling points of the metals are lower, the higher the atomic weight, and the specific gravity increases with the atomic weight.

	Melting point.	Boiling point.	Specific gravity.
Mg.	abt. 570° C	white heat	1·75
Zn.	430° C	1040° C	7·1
Cd.	320° C	860° C	8·5
Hg.	—39° C	350° C	13·59

3. The oxides have the general formula RO, the elements being divalent; they are much less pronounced in their basic character than those of the alkalies or alkaline earths, and form hydroxides which are readily transformed into oxides by heat, and are only slightly soluble in water.

4. The feeble affinity for acids is indicated by a marked tendency to the formation of basic salts, especially noteworthy in the case of the carbonates and the chlorides.

5. They form amides $R(NH_2)_2$, nitrides R_3N_2, and also combine directly with phosphorus to form phosphides.

6. They form no alums, but the chlorides and sulphates especially combine with alkaline chlorides and sulphates, and give rise to well-defined double salts, whose general formula is $MCl.RCl_2$ and $M_2SO_4.RSO_4$, where M is the alkaline element and R a member of this group.

MAGNESIUM.

Occurrence.—This element, although never found in nature uncombined, is yet one of the most abundant and widely distributed of the metals, being found as a constituent of many rocks and minerals. In the form of carbonate it occurs combined with calcium carbonate as the mineral dolomite or magnesium limestone, which is found in masses often several hundred feet in thickness. It is also found as carbonate in the form of magnesite, a mineral which crystallizes in rhombohedra, isomorphous with the crystals of calcite. As sulphate it occurs in sea water and in some mineral waters. Temporary hardness in spring water is sometimes due to the presence of magnesium salts in solution. In the neighbourhood of Stassfurt, large deposits of it are found in the form of kieserite $MgSO_4.H_2O$, a mineral which is employed in the preparation of magnesium sulphate or Epsom salts. As *chloride* it is found at Stassfurt in carnallite, a double chloride of potassium and magnesium, $KCl.MgCl_2.6\ H_2O$. It is also an essential constituent of many mineral *silicates*, the best known being hornblende, talc, asbestos, meerschaum, olivine and serpentine. Being so widely distributed, it is not surprising that it should be found in the tissues of plants and the bony parts of animals wherever lime salts are ordinarily present.

Metal.—Bunsen obtained the metal by the electrolysis of the fused chloride, but it is more usually prepared by heating the anhydrous mixture of potassium and magnesium chlorides (which results from fusing carnallite together with a little fluorspar in contact with sodium, and purifying the crude metal by subliming it).

The metal is of a lustrous white colour, it is malleable and can be obtained in coarse wire. It burns with great brilliancy when heated in air or oxygen or even at the expense of the oxygen in carbon dioxide, carbon separating out in the last case. Hot water is decomposed by it very slowly, but steam more rapidly. One of its most remarkable properties is the facility with which it combines with nitrogen; when heated in this gas it forms a yellowish-green amorphous *nitride* Mg_3N_2. Metallic magnesium is also, at high temperatures, a very powerful reducing agent, and there are very few oxides or compounds containing oxygen which are not either partially or entirely deprived of their oxygen when they are heated in contact with powdered magnesium.

The **oxide** $\mathbf{MgO}$ is obtained as a white powder when magnesium burns, or when the nitrate or carbonate is strongly heated. It is slightly soluble in water, to which it gives a faintly alkaline reaction. The *hydroxide* $Mg(OH)_2$ is obtained as a flocculent precipitate on adding caustic alkalies or baryta to a solution of magnesium chloride. The oxide is very infusible, and is used in the making of fire-bricks, and for pencils used in the Drummond light.

The **chloride** $\mathbf{MgCl_2}$ is formed by burning the metal in chlorine, or by the action of hydrochloric acid on magnesia or magnesium carbonate. From a concentrated solution, deliquescent crystals of the composition $MgCl_2.6H_2O$ separate out; the anhydrous chloride is difficult to obtain in the pure condition, for if heat be applied to get rid of the water of crystallization, some hydrochloric acid is given off and a basic chloride remains. When nearly all the water has been driven off at about 300° C., the basic salt is heated to bright redness and almost the whole of the remaining chlorine comes off chiefly in the free state, but partly combined with hydrogen as hydrogen chloride. Over 40 per cent. of the chlorine contained in magnesium chloride may be obtained as such, and hence this process has been worked with a view to the production of bleaching powder.

The *bromide* and *iodide*, $MgBr_2$ and MgI_2, are very soluble salts, resembling the chloride, and like it occurring in small quantity in sea-water, the peculiar bitter taste of sea-water being attributable to the presence of magnesium salts.

Magnesium sulphate, $MgSO_4$, is prepared, as already mentioned, from kieserite or by calcining dolomite or magnesian limestone (a mixture of lime and magnesia being thus obtained); the residue is exhausted with water to partially remove the lime, and then by the action of dilute sulphuric acid a solution is obtained from which on concentration magnesium sulphate crystallizes out. The salt is freely soluble in water, and when concentrated at ordinary temperatures it separates as $MgSO_4.7\,H_2O$ (Epsom salts), but at 30° C., $MgSO_4\,6\,H_2O$ is the product obtained. When saturated solutions of magnesium sulphate and the sulphate of potassium or ammonium are mixed together, crystals of the respective double salts $K_2SO_4\,MgSO_4.6\,H_2O$ and $(NH_4)_2SO_4.MgSO_4.6\,H_2O$ separate out.

Magnesium phosphate, $Mg_3(PO_4)_2$, is found in bones and in the tissues of plants; the double salt, $NH_4.MgPO_4.6\,H_2O$, is of importance as being almost insoluble in water, especially if a little ammonia be added. It is obtained by adding sodium phosphate to an ammoniacal solution of a magnesium salt; on ignition it is converted into magnesium pyrophosphate, $Mg_2P_2O_7$ and magnesium may be quantitatively estimated from the weight of the pyrophosphate obtained.

Magnesium carbonate, $MgCO_3$.—This occurs native as magnesite. When magnesium salts are precipitated by sodium carbonate, the composition of the product varies with the temperature and the proportions in which the reagents are mixed. Basic carbonates are, however, always formed, and from these the normal carbonate is obtained by digesting them with water in which carbon dioxide is dissolved. Sodium carbonate when added to a solution of magnesium sulphate in the cold yields a basic carbonate of the composition $Mg(OH)_2.4MgCO_3.9\ H_2O$, and from a boiling solution, *magnesia alba* $Mg(OH)_2.3MgCO_3.3H_2O$ is precipitated.

These bodies are almost insoluble in water, but in presence of ammonium salts a soluble double salt is formed, and hence ammonium carbonate fails to produce a precipitate in magnesium salts.

Detection and estimation.—Magnesium salts possess very few distinctive properties which can be used as means of identification. The carbonate although insoluble is not precipitated in presence of ammonium salts for the reason stated above.

In the course of analysis, all other elements except magnesium and the alkalies are first separated, and it is a question therefore of its detection in the presence of alkalies alone. The insolubility of the phosphate (the phosphates of the alkalies being soluble) affords a means of separation, the reagent used for its precipitation being sodium phosphate.

When heated on charcoal, magnesium salts like those of Zn, Al and the alkaline earths leave a white residue which glows brightly; this residue when moistened with nitrate of cobalt and again heated strongly shows a faint rose-colour. Magnesium is estimated as described previously in the form of pyrophosphate.

ZINC.

Occurrence.—The chief ores are the *sulphide*, called zinc blende or familiarly " black-jack," the *silicate*, known as electric calamine, and the *carbonate*, termed calamine.

Extraction from the ore.—This involves two main processes—

(*a*) Calcination or roasting.

(*b*) Reduction.

Calcination.—Calcination proper is employed in the case of calamine for the purpose of expelling the carbon dioxide and moisture. For zinc blende, the operation of roasting is performed, are being especially necessary to transform the sulphide as completely as possible into oxide and at the same time to avoid its passage into the sulphate.

Reduction.—Three processes have been largely used: (1) The English process, now entirely given up; (2) the Belgian process; (3) the Silesian process, mostly employed for poor ores. All these depend on coal or carbonaceous matter as the reducing agent, and they differ chiefly in the form and setting of the retorts used for working the charge and in the method of condensing the zinc.

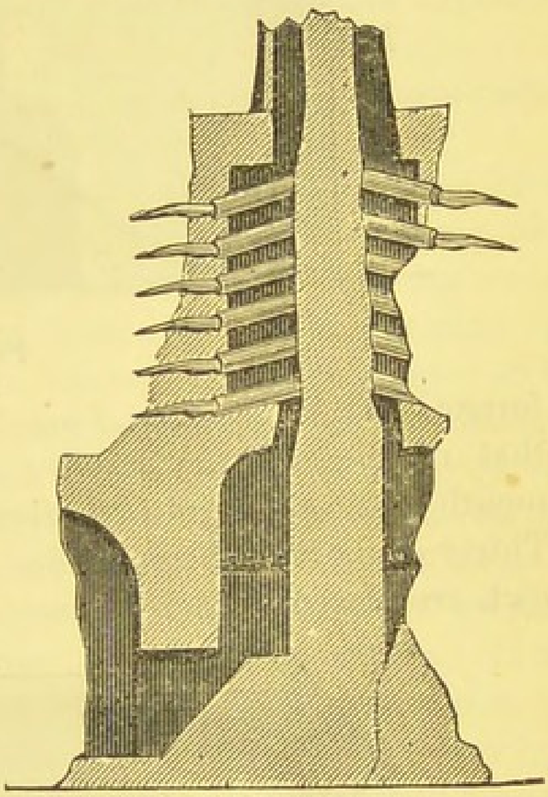


FIG. 29.

The Belgian process.—The retorts are of fireclay, circular or elliptical in section, about 3 feet 6 inches long and 9 inches wide, fitted at the mouth after charging with conical clay condensing tubes terminating in an iron nozzle. Thirty to forty of these retorts are arranged, sloping downwards towards the mouth, in a furnace as shown (Fig. 29). The charge, consisting of about two parts of the calcined ore (zinc oxide) to one of coal, both in powder and intimately mixed, is laid about 7 inches deep. A bright red heat is kept up for 24 hours and the oxide undergoes reduction, with the formation of carbon monoxide which burns at the mouth of the condenser.

$$ZnO + C = Zn + CO.$$

The temperature used being above the boiling point of zinc, the metal passes off in the form of vapour and condenses for the most part in the clay tubes. Zinc ores are always associated with cadmium, and this having a lower boiling point volatilizes first, producing brown fumes (oxide of cadmium), and the stage at which the zinc begins to distil is known by the flame at the mouth of the condenser changing to a greenish colour, and by the brown fume giving place to a white fume of zinc oxide. The extraction of zinc is accompanied by a loss of from 15 to 20 per cent. of the zinc.

Silesian process.—The retorts used are flat at the bottom and D shaped in section and both longer and deeper than those already described. The shape and their arrangement in the furnace will be evident from Figs. 30 and 31, the latter being that of the ordinary muffle; a curved tube passing from the mouth of the retort into a vertical cast-iron tube acts as condenser. Thirty or more of these muffles each having a charge of about 5 cwt. are placed in each furnace and heated by gas.

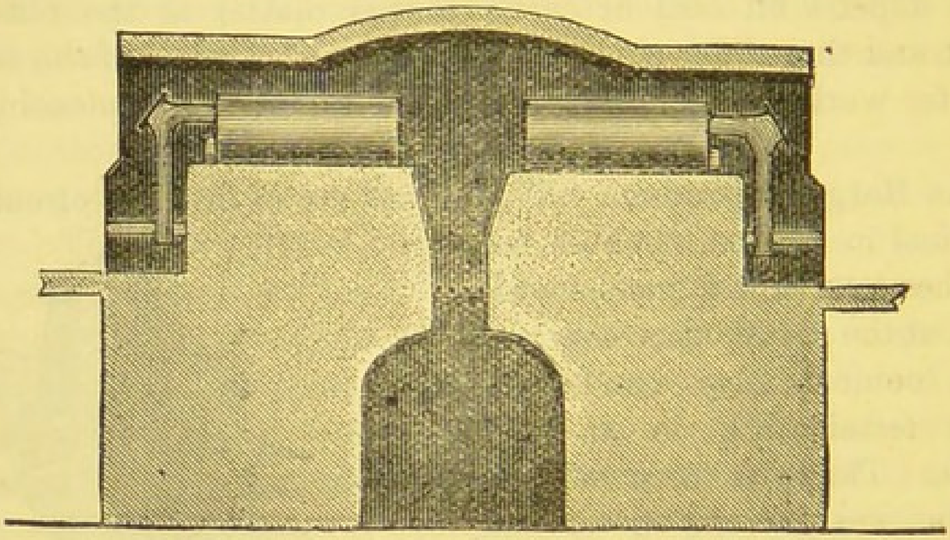


FIG. 30.

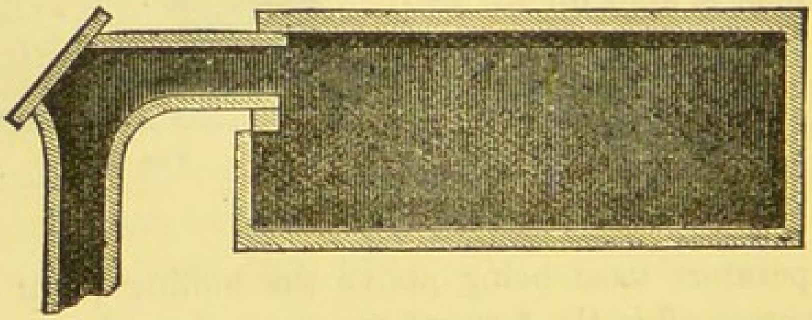


FIG. 31.

The **metal** is of a white colour with a bluish cast, brittle at ordinary temperatures, but at about 100° to 150° C. it becomes ductile and may be drawn into wire and rolled into sheet; above 200° C. it loses its cohesion and may readily be powdered. Commercial zinc contains traces of iron, cadmium, arsenic and sulphur; it dissolves freely in dilute mineral acids, and strong solutions of caustic alkalies with the evolution of hydrogen—

$$Zn + 2\,HCl = ZnCl_2 + H_2$$
$$Zn + 2\,KOH = \underset{\text{Potassium zincate.}}{K_2ZnO_2} + H_2$$

Water at its boiling point is decomposed by zinc. In the condensation of zinc a portion of the product is obtained in fine powder, known as zinc dust and frequently used as a reducing agent. Zinc is largely used for galvanizing iron plate which when dipped in the molten metal becomes coated with a thin layer of zinc and is thereby less liable to corrosion when exposed to the atmosphere.

Alloys.—The alloys which contain zinc are very numerous and find wide application.

The most important of these is brass, consisting of copper and zinc, the colour and other physical properties of which vary according to the proportions of its constituents. If it contains over 50 per cent. of zinc it is white and brittle, if over 80 per cent. of copper it is red or reddish yellow. Certain alloys of copper and zinc are known by special names, such as Muntz metal, pinchbeck, Dutch metal. German silver (and nickel silver) is an alloy of copper, zinc and nickel, and the English bronze coinage consists of 95 per cent. of copper, 4 per cent. of tin and 1 per cent. of zinc.

Zinc oxide, ZnO, occurs native as red zinc ore, the colour being due to the presence of iron or manganese oxides. It is formed as a white amorphous powder when zinc burns, which it does if heated somewhat above its melting point in air; also by strongly heating the carbonate or nitrate. It is used as a pigment under the name zinc white, the value of which consists in preserving its whiteness in presence of sulphuretted hydrogen (the sulphide being white) or other impurities in air.

The *hydroxide* $Zn(OH)_2$ is obtained by adding caustic alkalies to zinc salts; excess of the alkali re-dissolves the precipitate. In presence of caustic alkalies, zinc oxide may be regarded as playing the part of an acid-forming oxide, potassium zincate, K_2ZnO_2, being formed when zinc (especially in presence of iron) is heated with a strong solution of caustic potash.

Zinc sulphide, ZnS, is a white powder, the dark colour of the mineral, blende, being due to the presence of iron; in the hydrated form, it is obtained by the action of sulphuretted hydrogen or ammonium hydrosulphide on the neutral solution of a zinc salt. It is insoluble in acetic acid but soluble in mineral acids. A *pentasulphide* of zinc, ZnS_5, is obtained by adding potassium pentasulphide to a zinc salt.

Zinc amide, $Zn(NH_2)_2$, is formed by acting on zinc ethyl with dry ammonia—

$$Zn(C_2H_5)_2 + 2\,NH_3 = Zn(NH_2)_2 + 2\,C_2H_6.$$

Water decomposes it—

$$Zn(NH_2)_2 + 2\,H_2O = Zn(OH)_2 + 2\,NH_3$$

and by heat it is transformed into a green powder, the *nitride* of zinc, Zn_3N_2—

$$3\,Zn(NH_2)_2 = Zn_3N_2 + 4\,NH_3.$$

A *phosphide* of similar composition is obtained by the direct union of zinc and phosphorus.

Zinc chloride, $ZnCl_2$.—This, as well as the bromide and iodide, may be prepared by the interaction of zinc with the halogen element, or by the action of the halogen acid on the metal, oxide or carbonate. It is extremely soluble in water, even one-third of its weight of water sufficing to produce a thick oily liquid, from which on evaporation the anhydrous substance is obtained as a white solid. It is very deliquescent, and hence a powerful dehydrating agent, attacking many organic substances with the abstraction of water. By boiling its solution with zinc oxide, oxychloride of zinc is formed.

Zinc sulphate, $ZnSO_4$, known also as white vitriol, is formed by the action of sulphuric acid on zinc or its oxide or carbonate; also by roasting zinc blende. Three parts of water dissolve four parts of the salt at ordinary temperatures, and on concentration of the solution it separates out in crystals, having the composition $ZnSO_4 7\,H_2O$.

Zinc carbonate, $ZnCO_3$, occurs, as already stated, in the form of calamine. On the addition of $KHCO_3$ to a zinc salt this (the normal) carbonate is precipitated, but if K_2CO_3 be used, basic carbonates of variable composition are obtained according to the temperature at which the experiment is carried out or the amount of water present.

Detection and estimation.—Zinc salts do not ordinarily impart colour to the Bunsen flame, but the acetate gives a peculiar bluish-green colour. The spark spectrum is a complex one, the more distinctive lines being those of wave length 6362 and 6099 in the red, and a triplet 4928, 4924, 4911 in the blue. Characteristic features are—

(1) The formation of a white sulphide (soluble in mineral acids, insoluble in acetic acid), by the action of sulphuretted hydrogen or soluble sulphides.

(2) The precipitation of the hydroxide by caustic alkalies, soluble in excess.

(3) The white residue (luminous when hot) left on charcoal when zinc salts are strongly heated, and the green colour which appears when this residue is heated after the addition of cobalt nitrate.

Zinc is usually estimated in the form of oxide, the basic carbonate being first precipitated by means of sodium carbonate, and this converted into the oxide by strong ignition.

CADMIUM.

Occurrence.—Cadmium is predominant in a few minerals, *e. g.* Greenockite, CdS, but the bulk of it is found accompanying zinc ores, the extraction proceeding alongside that of zinc.

The **metal** is quite white and fibrous; it can be rolled into sheet or drawn into wire, and though it melts at 315° C., it is found that when one part of it is alloyed with bismuth four parts, lead two parts, and tin one part, the product melts at 61° C. This is called Wood's metal.

The **oxide, CdO,** is of a rich brown colour, and is observed during the distillation of zinc ores, and also as an incrustation when cadmium salts are heated on charcoal. The *hydroxide* is, like zinc hydroxide, obtained by the addition of caustic alkalies to its salts; it absorbs carbon dioxide on exposure to air in the moist condition.

The **salts of cadmium** show very great resemblance to those of zinc; the normal carbonate is unknown, the precipitate obtained by alkaline carbonates being always a basic carbonate of variable composition.

The **sulphide** of cadmium is of a bright yellow colour, soluble in moderately concentrated mineral acids; it is formed when sulphuretted hydrogen is passed through a solution of a cadmium salt. Sulphide of cadmium may be separated from sulphide of copper by digestion with dilute sulphuric acid (one part of acid to five of water), the sulphide of cadmium being dissolved; also from a mixture of the sulphides of zinc and cadmium, the former may be dissolved out by very dilute sulphuric acid.

Detection and estimation.—The detection of cadmium is based on—

(1) The formation of a brown incrustation on charcoal.

(2) The precipitation as a yellow sulphide, insoluble in dilute acids.

The estimation is made either as sulphide or as oxide, the methods being similar to those used with zinc.

MERCURY.

Occurrence.—Although occasionally found in small quantity in the free state, the sulphide, HgS, cinnabar, is by far the most important source of mercury. The chief localities where the extraction is carried on are Idria in Austria, Almaden in Spain, and in the neighbourhood of San Francisco, California.

Extraction from the ore.—The process of extraction is an extremely simple one, and consists usually in roasting the ore in a reverberatory furnace, or even a small blast furnace, with access of air by which the sulphur is oxidized to sulphur dioxide, and the mercury set free and volatilized.

$$HgS + O_2 = Hg + SO_2.$$

Sometimes lime or oxide of iron ("smithy scales") are mixed with the ore, and the sulphur retained in this way as sulphide of lime or iron respectively. The condensation of the vapours of mercury is, however, a matter of some difficulty, and the methods employed vary considerably in the different localities.

At Idria, the vapours are passed through chambers, and a series of twin tubes of cast-iron cooled externally by water. They are so arranged that the condensed metal collects, and runs down into the receptacle at the base of each tube. In Almaden, twelve parallel series of conical clay receivers called "aludels," luted together, are interposed between the furnace and the flue; each of these is about twenty inches long, and a series extends about twenty yards. The lines of aludels are of sufficient length to allow the vapours and gases to cool down nearly to the temperature of the air, and so arranged as to allow the condensed mercury to gravitate towards a common channel where it collects.

The **metal** thus obtained contains small quantities of lead, bismuth, zinc, etc.; it may be purified by distillation in vacuo, or by treatment with dilute nitric acid, which dissolves out the impurities. It has a specific gravity of 13·596, and is the only metal that is liquid at the ordinary temperatures; it possesses a silvery lustre; at − 39° C. it becomes solid, and in this form it is malleable. Even at ordinary temperatures it has a small vapour tension, and gives off minute quantities of its vapour into the atmosphere in contact with it; at about 360° C. it boils, and is entirely transformed into vapour, the molecule of which is monatomic (see page 16). When heated almost to its boiling point in air it becomes coated with the red oxide, HgO; ozone oxidizes it superficially at ordinary temperatures.

Amalgams.—With most of the metals it forms alloys (amalgams), and in some cases these amalgams possess a definite composition, and crystalline form, *e. g.* Hg_5Na is brittle, and crystallizes in the regular system. Sodium amalgam is a convenient reducing agent, for when brought into contact with water or solutions in water, hydrogen is evolved. Tin amalgam is used for producing the silvery coating on glass for mirrors.

Mercury forms two series of compounds, the *mercurous* in which it is monovalent, and the *mercuric* in which it is divalent. It will be seen that the two series differ very considerably in properties.

Mercurous oxide, Hg_2O, is a dark brown powder obtained by digesting calomel ($HgCl$) with caustic potash; it is unstable, and is even decomposed by the action of light with the production of mercuric oxide and metallic mercury.

Mercuric oxide, HgO, exists as a crystalline red powder obtained by heating the metal in air, or by calcining the nitrate. It is also obtained as a yellow powder by the addition of caustic alkalies to mercury salts, and in this form by reason of its finely divided state, and the readiness with which it parts with oxygen, the oxide is an active oxidizing agent.

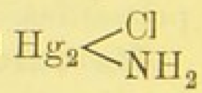
Mercuric sulphide, HgS, is formed as a black powder by triturating mercury and sulphur together, or by precipitating solutions of mercuric salts with sulphuretted hydrogen. It occurs also as a bright red powder, the pigment vermilion. This is prepared either by the *dry process* in which a mixture of mercury and sulphur is heated, or by the *wet process,* in which amorphous sulphide of mercury is exposed to action of alkaline sulphides. Exceptional brightness of tint and degree of fineness are attained only by attention to technical detail in the preparation.

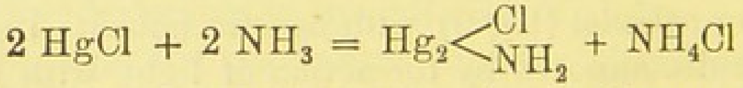
Mercury nitride, Hg_3N_2.—This body is obtained by gently heating (to about 130° C.) dry yellow mercuric oxide in a current of gaseous ammonia,—

$$3\ HgO + 2\ NH_3 = Hg_3N_2 + 3\ H_2O.$$

By the action of dilute ammonia on yellow mercuric oxide, Millon's base is formed; this body has the composition $NHg_2.OH_2.OH$, and by gently heating, it is transformed into the anhydrous $(NHg_2)_2O$. These substances in the dry state are very unstable and liable to decompose with explosion, yet they are so strongly basic as to resemble the caustic alkalies, expelling ammonia from its compounds, absorbing carbon dioxide very freely and only undergoing decomposition when fused with potash or soda. $NHg_2.OH_2.OH$ forms a well-defined series of salts in which the OH group is replaced by the acid radical.

This tendency to form ammonia-bases and salts containing the amido-group NH_2 is particularly characteristic of mercury.

Thus mercurous chloride, $HgCl$, is by the action of aqueous ammonia transformed into the black amido-compound  $Hg_2\Big<\genfrac{}{}{0pt}{}{Cl}{NH_2}$



$$2\ HgCl + 2\ NH_3 = Hg_2\Big<\genfrac{}{}{0pt}{}{Cl}{NH_2} + NH_4Cl$$

and mercuric chloride, $HgCl_2$, is likewise acted upon by aqueous ammonia forming the body termed *infusible white precipitate*, $Hg<^{Cl}_{NH_2}$

$$HgCl_2 + 2\,NH_3 = Hg<^{Cl}_{NH_2} + NH_4Cl$$

Ammonia also forms additive compounds such as Hg_2Cl_2 $2\,NH_3$ and $HgCl_2.2\,NH_3$, the latter being known as *fusible white precipitate*. Similar derivatives are obtainable with other salts of mercury.

Mercurous chloride or calomel, HgCl.—Is found as the mineral horn-quicksilver and produced artificially like the other mercurous haloid salts—

(1) By the direct union of mercury with chlorine.

(2) By the addition of the hydrochloric acid, or a soluble chloride to a solution of a mercurous salt.

(3) By the action of certain reducing agents such as phosphorous acid or stannous chloride on mercuric chloride.

(4) By triturating mercuric chloride with metallic mercury.[1]

Calomel is an amorphous white powder insoluble in water and acids; it can be brought into solution (as *mercuric* chloride) by the action of strong nitric acid or aqua regia or by prolonged digestion with the dilute acid. If heated alone it sublimes, but in contact with carbon it undergoes reduction to metallic mercury.

Mercuric chloride, corrosive sublimate, $HgCl_2$.—Corrosive sublimate is made on the large scale by heating 5 parts of mercuric sulphate with 2 parts of common salt

$$HgSO_4 + 2\,NaCl = HgCl_2 + Na_2SO_4$$

and finally separating the mercury salt by sublimation.

It is readily soluble in water, alcohol or ether, and in presence of hydrochloric acid or alkaline chlorides, it forms double salts such as $HgCl_2.3HCl$ and $HgCl_2.2NH_4Cl.H_2O$. It also shows the tendency characteristic of this group of elements to form oxychlorides, which are obtained by digesting the solution with mercuric oxide.

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[1] It may in general be taken that in the preparation of salts of mercury, if the metal be kept in excess the *mercurous* salt is obtained, whilst if the acid be concentrated and in excess the *mercuric* salt will be obtained, and that the latter will be converted into the former by trituration with excess of the metal.

It crystallizes from a hot solution in needles which melt at 288° C. and at about 300° C. become transformed into vapour. The compound is extremely poisonous but in small doses it is a valuable medicine; its solution possesses also powerful antiseptic properties.

Mercurous iodide, HgI, or mercuric iodide, HgI_2, are obtained by triturating mercury and iodine together, the former resulting when excess of mercury is used, and the latter if the iodine is in excess. Mercuric iodide is also obtained as a brilliant red precipitate, by mixing solutions of potassium iodide and mercuric chloride, the precipitate being soluble in excess of either reagent. If the potassium iodide be added until the red precipitate is just redissolved and then caustic soda, *Nessler's solution* is obtained, and this is an extremely sensitive reagent for detecting the presence of ammonia. Minute traces of ammonia give a yellowish brown colouration and greater quantities yield a brown precipitate.

The scarlet iodide of mercury when heated passes into a bright yellow form, which is however unstable and returns to the red form again, slowly on standing, or immediately by rubbing it.

Mercuric cyanide, $HgCy_2$, is of importance as being the salt which on heating yields cyanogen gas. It is prepared by boiling mercuric sulphate and potassium ferrocyanide together in aqueous solution. It crystallizes in white needles and is soluble in about 8 parts of cold water.

Mercurous sulphate, Hg_2SO_4, or mercuric sulphate, $HgSO_4$, are obtained by heating together mercury and sulphuric acid according as excess of mercury or sulphuric acid respectively is used. The mercuric sulphate is the more important salt; it consists of white crystals which on heating undergo decomposition with the formation of mercurous sulphate. In presence of water the salt is very liable to become basic; *turpeth mineral* is a yellow basic sulphate, $2\,HgO.Hg_2SO_4$, obtained by digestion with boiling water.

Mercurous nitrate, $HgNO_3$, and mercuric nitrate, $Hg(NO_3)_2$, are formed from mercury and nitric acid under similar conditions to the sulphates and like them form basic salts in presence of water.

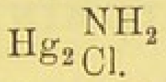
For the weaker acids the affinity of mercury is too small to admit of the formation of stable salts; the phosphates, carbonates, borates and silicates have been either not prepared at all or obtained as basic compounds of variable composition.

Detection and estimation.—The most reliable method of detection consists in obtaining from its compound metallic mercury, which is easily recognized. This may be done either—

(1) By reduction in contact with sodium carbonate, lime or carbon in a bulb tube, or

(2) By digestion with stannous chloride when the mercury is obtained in minute grey globules.

$$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$

Mercurous salts are precipitated on the addition of hydrochloric acid or a soluble chloride as calomel which by the addition of ammonia turns black, forming  $Hg_2\begin{matrix}NH_2\\Cl\end{matrix}.$

Mercuric salts are not precipitated by these reagents, but yield when treated with sulphuretted hydrogen the black sulphide, HgS, insoluble in dilute acids. This sulphide is separated from the sulphides of Cu, Pb, Bi which are also black and insoluble in dilute acids by its insolubility in nitric acid.

The quantitative estimation of mercury is made either by igniting the compound with lime and weighing the mercury which distils over or by the action of phosphorous acid on mercuric chloride and weighing the calomel so produced.

CHAPTER XI.

ALUMINIUM.

Occurrence.—In combination with oxygen as alumina or as complex minerals in which alumina enters as one of the constituents, the distribution of this element is a very wide one. Clays of all kinds consist essentially of silica and alumina in varying proportions associated with smaller quantities of lime, magnesia and oxides of iron or of the alkalies. The felspars are similar in general composition to clay but each possesses its own proper crystalline form and more or less definite amounts of the constituent oxides ; orthoclase for instance is essentially $K_2O.Al_2O_3.6\ SiO_2$.

Kaolin is a white clay which results from the decomposition of felspar and consists of a hydrated silicate of alumina, $Al_2O_3.2\ SiO_2.2\ H_2O$.

Alumina itself occurs as bauxite, corundum, emery and the precious stones, ruby, amethyst, sapphire, topaz, the colour of these bodies being due to the presence of oxides of iron, cobalt, or chromium. Cryolite is the double fluoride of sodium and aluminium $6\ NaF.Al_2F_6$. and the spinelles are aluminates of zinc or magnesium $RO.Al_2O_3$.

Metal.—Since 1827, when Wöhler first prepared metallic aluminium, many processes have been suggested from time to time, but most of them are only adapted for the preparation of the metal in small quantities. The methods which have been successful on a large scale may be classed under two heads—

(1) Those in which a haloid salt or double salt of aluminium is reduced by being heated with metallic sodium.

(2) Those in which aluminium (or its alloys) is obtained by the electrolysis of alumina or its haloid salts.

Reduction process.—The material used for this purpose must be free from iron, and bauxite is a mineral form of alumina which contains little oxide of iron; even this, however, must be removed. This is done by heating the bauxite in kiers with a solution of caustic soda, by which sodium aluminate is formed, and may be separated from the oxide of iron by lixiviation with water—

$$Al_2O_3 + 6\ NaOH = 3\ Na_2O.Al_2O_3 + 3\ H_2O.$$

The solution of aluminate is then exposed to a current of carbon dioxide, the reaction which then occurs is—

$$3\ Na_2O.Al_2O_3 + 3\ CO_2 = Al_2O_3 + 3\ Na_2CO_3$$

The separation of the alumina (as hydroxide) may also be effected by digesting the sodium aluminate with an excess of alumina, and this process is now more usually adopted.

The alumina is mixed with common salt and charcoal, the mixture is dried and then exposed at a red heat to dry chlorine; aluminium chloride, Al_2Cl_6, is produced and this combines with excess of the salt and forms the double salt $2\ NaCl.Al_2Cl_6$, the product which is most advantageously reduced by sodium.

The reducing operation is carried on at red heat in a reverberatory furnace, the charge consisting of 11 parts of the double salt mixed with 4 parts of sodium and 5 parts of cryolite added to serve as a flux.

The reaction is a violent one for about a quarter of an hour and at the end of three hours the reduction is finished. The aluminium collects on the bed of the furnace beneath the slag, and after the latter is run off the metal is drawn and run into moulds.

The electric process.—This method was at first used only for the production of alloys of aluminium. The charge consists of corundum (Al_2O_3) (or the alumina obtained as above) 25 parts, carbon, 12 parts, and metallic copper, 50 parts, and is placed in a rectangular box; the electrodes are carbon rods 3 inches thick or a group of several thinner rods. The current is furnished by a powerful dynamo and to begin with the electrodes are brought near together, the charge offering a very high resistance. Much heat is developed and the part of the charge in proximity to the electrodes fuses, thereby the resistance decreases and the carbon rods can be drawn further apart. Ultimately the whole charge is fully heated and in five hours the reduction is complete, the copper-aluminium alloy which results containing 15 to 30 per cent., or even more, of aluminium. By using alumina with the addition of fluoride to act as a flux, which thus enables the charge to conduct, it has been found that aluminium may be obtained.

The manufacture of aluminium on these lines has been established by the British Aluminium Company at Foyers ; water power is available for running the dynamos, the cost being thus reduced to about one-third of what it would be if coal were used.

The operation is carried out in an iron box lined with carbon, constituting the *cathode*, whilst the *anode* consists of a bundle of carbon rods which extend nearly to the bottom of the box. Part of the energy of the current employed has a tension of 3 to 5 volts, and part of the energy is utilised in keeping the cryolite molten (the temperature of the bath being about 800° C), the remainder in electrolysing the alumina. The cryolite itself does not undergo decomposition, but continual additions of alumina have to be made to replace that which has undergone reduction to the metallic form. By such appliances the cost of production of aluminium has been reduced to little over one shilling per pound, whereas the Deville process came to about sixty shillings per pound.

Aluminium is a white metal with a bluish tinge, it is remarkable for its lightness, its sp. gr. being about 2·6 ; it melts at 600° C. Its lightness, great tensile strength (about ⅓ that of steel) and malleability render it a most useful metal. It is almost unacted upon by acids, except the halogen acids, but alkalies attack it rapidly. In the finely divided state or in thin foil it burns readily when heated in air or oxygen, but in mass, oxidation only occurs at a white heat.

Alloys.—With copper, aluminium forms alloys in all proportions and the products are valuable partly for their colour (aluminium gold) and partly for their tensile strength and resistance to corrosion. Aluminium bronze (90 pts. of copper to 10 pts. of aluminium) is one of the most valuable of these alloys; its tensile strength is equal to that of good steel, it has a golden colour and takes a high polish.

An alloy of aluminium with 10 per cent. of tin possesses most of the valuable properties of brass, whilst it is much lighter and less easily corroded than brass. The addition of small quantities, even $\frac{1}{10}$ per cent., of aluminium to steel increases its fluidity and lowers its melting point so that it can be rendered more dense and obtained much more free from bubbles of gas by the hydraulic pressure to which it is subjected whilst molten.

The oxide, alumina, Al_2O_3, and **the hydroxide, $Al_2(OH)_6$.**— The hydroxide is precipitated from solutions of the salts by caustic alkalies (soluble in excess), ammonia or ammonium carbonate. It is also precipitated from alkaline aluminates by carbon dioxide. (See p. 181.)

Some of the less stable salts of aluminium, such as the acetate, decompose with the separation of the hydroxide when the solution is boiled. The hydroxide as formed by any of these methods is a bulky flocculent precipitate which carries down with it certain colouring matters, and if a fabric be first charged with suitable salts of aluminium and then brought into a dye-bath the colouring matter is carried on to the fibre and fixed there. Salts which act in this way are called *mordants* from the property which they possess of fixing the colours on cloth.

The freshly precipitated hydroxide is readily soluble, even in dilute acids, but it slowly passes at ordinary temperatures, and more rapidly on boiling, into a form which is difficultly soluble. This seems to be due to the loss of water of hydration, the ordinary hydroxide $Al_2O_3.3\,H_2O$ passing into $Al_2O_3.2\,H_2O$ or $Al_2O_3.H_2O$. By igniting the hydroxide, the whole of the water is driven off and the anhydrous oxide Al_2O_3 obtained as a pulverulent white powder. This is only slowly acted upon even by concentrated mineral acids, and the crystalline forms of alumina, such as corundum and emery, are absolutely insoluble in acids. By exposing a dilute solution of aluminium acetate, or one containing the basic chloride of aluminium in a dialyser, the acid slowly passes through the membrane and leaves a solution of aluminium hydroxide in water in the colloidal condition, and this coagulates on the addition of small quantities of alkalies, acids or certain salts.

We recognize thus—

(1) The colloidal form ($Al_2O_3\ x\ H_2O$), soluble in water.

(2) The precipitated form ($Al_2O_3.3\ H_2O$), soluble in dilute acids.

(3) The precipitated form ($Al_2O_3.H_2O$), ? insoluble in dilute acids.

(4) The crystalline form (Al_2O_3), insoluble even in strong acids.

Aluminium sulphide, Al_2S_3, is obtained by heating aluminium to redness in contact with sulphur ; it can only be prepared in the dry way and decomposes when brought into water forming the hydroxide. When, therefore, solutions of aluminium salts are treated with alkaline sulphides, the precipitate formed consists of the hydroxide.

Aluminium fluoride, Al_2F_6, is obtained by acting on aluminium with silicon tetrafluoride ; it is quite insoluble in water and acids. By digesting aluminium hydroxide in excess with sodium fluoride, the double fluoride 6 $NaF.Al_2F_6$ is obtained ; it is also found native as cryolite.

Aluminium chloride, Al_2Cl_6, is prepared by heating the metal or a mixture of alumina and carbon in chlorine. It can be readily sublimed, as it volatilizes at 183° C. Below 400° C. its vapour density is such as to agree with the formula Al_2Cl_6, but at higher temperatures the density agrees with $AlCl_3$. It is a white deliquescent substance which shows a great tendency towards the formation of double salts, combining directly with ammonia, phosphorus pentachloride and oxychloride, and with alkaline chlorides. The double salt $2NaCl.Al_2Cl_6$ was employed by Deville in contact with sodium for the production of aluminium but is now no longer used for this purpose.

Aluminium sulphate, $Al_2\ (SO_4)_3$.—This salt is prepared on the large scale by treating bauxite with sulphuric acid. It crystallizes at low temperature with 16 H_2O. The solution of the salt possesses a marked acid reaction, and in presence of zinc, hydrogen is evolved and basic sulphates are formed; regarding the original sulphate as $Al_2O_3.3\ SO_3$, these basic sulphates have the composition $Al_2O_3, 2\ SO_3$, and $Al_2O_3SO_3$ respectively. Aluminium sulphate is used in dyeing and calico printing and also as a precipitant for the treatment of sewage. When it is mixed with sulphates of the alkalies, the crystals which separate out are double salts known as the alums.

The alums have the general composition—

$M_2SO_4.R_2(SO_4)_3.24\ H_2O$ where M is K, Na, NH_4, Rb, Cs, Tl or Ag, and R may be Al, Cr or Fe, Ga, In.

The alums crystallize readily in octahedra and are much more soluble in hot water than cold; 100 parts of water dissolve of potash alum—

at 0° C.	30° C.	70° C.	100° C.
4 pts.	22 pts.	91 pts.	357 pts.

Alum-stone is a double salt of potassium sulphate and basic aluminium sulphate $K_2SO_4.Al_2(SO_4)_3 2.Al_2(OH)_6$ found in volcanic regions. It is insoluble in water until it has been heated to dull redness (about 450° C.); water then acts upon it and alum passes into solution, whilst alumina separates out. The alum obtained in this way (known as Roman alum) crystallizes in cubes and is valuable from the fact that it is almost entirely free from iron, iron salts being detrimental to the use of alum in dyeing and printing. In recent years, methods have however been introduced by which aluminium compounds free from iron may be prepared from bauxite or alum clays.

Aluminium nitrate, $Al_2(NO_3)_6$, is prepared by dissolving freshly precipitated hydroxide of aluminium in nitric acid or by the precipitation of lead nitrate with aluminium sulphate just sufficient to convert the whole of the lead into the insoluble sulphate—

$$3\ Pb(NO_3)_2 + Al_2(SO_4)_3 = 3\ PbSO_4 + Al_2(NO_3)_6.$$

It is used as mordant for alizarin colours in calico printing.

Aluminium silicates.—Shale and many important minerals consist essentially of these silicates, and clays result from the weathering of such bodies. The composition of some well-known clays is given below—

	Alumina.	Silica.	Ferric oxide.	Lime and Magnesia.	Alkalies.	Water.
Kaolin (Cornwall)	38·6	46·4	—	3·5	1·8	9·1
Stourbridge fire-clay	23·3	63·3	1·8	0·7	—	10·3
Common clay, used for brick making	34·3	49·4	7·7	3·4	—	5·1
Clay for porcelain	36·8	46·8	1·0	2·6	0·3	12·4
Clay for glass making	18·8	72·0	1·7	0·7	0·1	6·7

In the process of firing clay for the production of bricks, pottery or porcelain, the material used undergoes a partial fusion whereby the particles become cemented together in a firm vitreous mass. The clay is in general the more infusible the larger the proportion of alumina and silica bears to that of alkalies and basic substances. Bricks for furnace linings (fire-bricks), which must withstand very high temperatures, are thus made from clay which is almost entirely composed of alumina and silica, whilst glass, in which the materials are actually brought into a state of liquid fusion, is produced from a siliceous product to which alkalies and other basic substances are added in considerable quantity. The special nature of the additions varies according to the purpose for which the glass is to be used.

The composition of a number of different forms of glass as given in the following table will illustrate this—

	Silica.	Potash.	Soda.	Lime and Magnesia.	Lead Oxide.	Alumina and oxide of iron.
Ordinary bottle glass	65·6	2·7	4·9	20·4	—	6·1
Window glass ...	70·7	—	13·3	13·4	—	1·9
Flint glass ...	50·2	11·2	—	—	38·1	0·5
Fusible glass for chemical apparatus	70·5	2·1	17·2	8·7	—	1·0
Infusible glass for combustion tubes	73·1	11·5	3·1	10·7	—	0·9

The temperature employed in the firing of bricks or pottery varies from a bright red heat in the case of bricks and tiles to a bluish-white heat, somewhat above the melting point of grey cast-iron, for porcelain. The glaze on pottery is a thin layer of a mixture of a more fusible character than the pottery itself; it usually consists of mixtures of sand and alkalies, to which oxides of lead or (for enamels) tin may be added. The colours of glass are due to the presence of certain metallic oxides. Oxide of iron gives it a green colour, as in bottle glass; oxide of manganese gives it a pink colour, and is sometimes added to correct the green tint given by oxide of iron; oxide of cobalt gives a blue colour, oxide of chromium or cupric oxide, green; cuprous oxide, or gold, ruby red. The addition of oxides of tin or antimony as well as bone ash gives rise to the opaque enamel appearance in glass.

Ultramarine is an artificial colouring matter whose chief constituents are—

Alumina	25 to 28	per cent.
Silica	38 to 45	,,
Soda	18 to 23	,,
Sulphur	10 to 14	,,

It is obtained by exposing a mixture of kaolin, sodium sulphate, and coal to a bright red heat in closed fire-clay crucibles. Though usually applied to a bright blue colouring matter, artificial ultramarine may be prepared of different tints. The product obtained as the immediate result of the operation just mentioned is of a *bright green* colour, but this when treated with sulphur dioxide at 300° C. turns *blue*. If air be scrupulously excluded from the crucible, *white* ultramarine is obtained, and by the action of chlorine and steam at 200° C. a *violet* modification is formed, or with hydrochloric acid at a somewhat lower temperature the product is of a *rose red* colour.

The composition of ultramarine varies according to the proportions of the constituents used in its manufacture; if it is poor in silica, its colour is readily destroyed by acid substances, and hence in calico printing and paper manufacture, where it is liable to come into contact with alum, a product rich in silica is used.

Detection and estimation.—In the dry way the salts of aluminium when strongly ignited leave a white residue of alumina which in the blowpipe-flame glows brightly. This mass when moistened with a solution of cobalt chloride and again ignited gives a bright blue residue. The hydroxide is precipitated from solutions of the salts by ammonia or ammonium carbonate, and separated from ferric hydroxide by caustic potash in which it readily dissolves.

The presence of certain organic acids, such as citric and tartaric, prevents the precipitation, owing to the formation of soluble double salts with these acids. Aluminium is always estimated in the form of alumina obtained by igniting the precipitated hydroxide.

CHAPTER XII.

THE NOBLE METALS.

Cu, Ag, Au, and as sub-group the Platinum metals.

General characters.—

1. The metals are the most malleable and ductile known, and also the best conductors of heat and electricity.

2. They possess small affinity for oxygen and are weak bases, the basic character also decreasing as the atomic weight rises. They are hence found native in the free state. They do not decompose water even at high temperatures.

3. Copper, silver, and gold may be regarded as standing midway between the group zinc, cadmium, and mercury, and the group nickel, palladium, and platinum. Further, these metals occupy a similar relation to the alkalies that zinc, cadmium, and mercury do to the alkaline earths.

4. Additive compounds with ammonia are frequent in this group, instances of which are—

$2\,AgCl.3\,NH_3$	$Ag_2SO_4.2\,NH_3$	$AgNO_3.2\,NH_3$
$CuCl.NH_3$	$CuSO_4.4\,NH_3$	$Cu(NO_3)_2.4\,NH_3$.

Copper, silver, and gold form nitrides of the composition R_3N, but of small stability. The stability of the ammonia and nitrogen compounds is smaller the higher the atomic weight.

5. They form double salts with the alkalies, those with the haloid salts and cyanides being especially characteristic. Instances of these are—

$KCl.CuCl$	$2\,KCl.CuCl_2$	$Na_2Cu(CO_3)_2$
$KCl.AuCl$	$KCl.AuCl_3$	$KAg.CO_3$.

The double cyanides have the composition—

$\mathrm{MCy.R'Cy}$ with Cu, Ag, Au
2 $\mathrm{MCy.R''Cy_2}$ „ Ni, Pt
3 $\mathrm{MCy.R'''Cy_3}$ „ Co (and Fe)
4 $\mathrm{MCy.R''Cy_2}$ „ Fe.

It is thus seen that platinum and its analogues which enter into the formation of these double cyanides arrange themselves in accordance with the Mendelejeff classification.

COPPER.

Occurrence.—Copper is found as the *metal* in considerable quantity in the neighbourhood of Lake Superior, also in smaller amount in some other parts of the American continent, in Cornwall, and in Siberia and the Ural mountains; as *cuprous oxide*, Cu_2O, in the mineral cuprite it is found in Cornwall, South America, and Australia; as *cuprous sulphide*, Cu_2S, in copper glance, and associated with sulphide of iron in copper pyrites; as *basic carbonate* in malachite, $CuCO_3.Cu(OH)_2$, and in azurite, $2\ CuCO_3.Cu(OH)_2$. In addition to these minerals, which are used for the extraction of copper on the large scale, mineral silicates, phosphates, arsenates, and oxychloride are known. Copper is also found in the colouring matter of the red wing-feathers of certain birds.

Metallurgy of copper.—In practice, the process of extraction of copper is a very complex one, entailing a large number of operations. We shall describe first the chemical reactions involved, and then the essential operations by which metallic copper is ultimately obtained from a mixture of copper sulphides and oxidized ores, such as are most commonly employed in this country.

Chemical reactions.—Copper possesses a greater affinity for sulphur and a smaller affinity for oxygen than the metals (notably iron) with which it is associated.

(1) The ore is first moderately heated in a reducing atmosphere; part of the sulphur and arsenic are oxidized, and pass off as sulphur dioxide and arsenic trioxide respectively. This operation is regulated so that the sulphur retained is sufficient to

combine with the whole of the copper to form cuprous sulphide, Cu_2S, the iron and part of the copper being transformed into oxide. The charge is then brought to fusion at a higher temperature, when the ferrous oxide enters into combination with the silica, either already contained in the ore or added to the charge, to form a slag of ferrous silicate. By repetition of the roastings and fusions the iron is ultimately removed.

(2) At a moderate temperature the cuprous sulphide is then partially oxidized, and the temperature is raised so that the cuprous oxide formed may react with the sulphide—

$$2\ Cu_2O + Cu_2S = 6\ Cu + SO_2.$$

The remainder of the sulphur is thus eliminated and metallic copper obtained. Any sulphide of iron which still remains is also acted upon by the cuprous oxide as follows—

$$3\ Cu_2O + FeS = 6\ Cu + FeO + SO_2.$$

(3) The crude copper so obtained is further refined by a process which is described below.

The operations.—

1. *Calcination.*—This is performed either in heaps or on the bed of a reverberatory furnace. In the former the ore is made into heaps, the height of which varies according to the richness of the ore, being for rich ores about 5 feet, and for poor ores about 7 feet. The heat requisite is obtained by the firing of logs of wood placed in a layer in the lower part of the heap, vents being provided so that a sufficient supply of air may be brought into contact with the ore. The main objects of this calcination are the removal of part of the sulphur and the volatilization as completely as possible of any arsenic or antimony present in the ore, as these substances are most prejudicial to metallic copper. If the calcination is carried out in a reverberatory furnace (Figs. 33 and 34) the chief provisions to be attended to are a low temperature (secured by having the fire-grate, F, small in proportion to the bed of the furnace, B, viz. 1 to 15 or 20), and properly regulated air supply admitted at A. The charge is introduced at the hoppers, C, and spread over the bed of the furnace, being worked from the doors, D, and finally withdrawn through openings, E, in the bed of the furnace, and shot

down into the vault, G, the course of the discharge exits being shown by dotted lines in Fig. 33.

2. *The fusion.*—A higher temperature is required for this process, which is therefore carried out in a reverberatory furnace

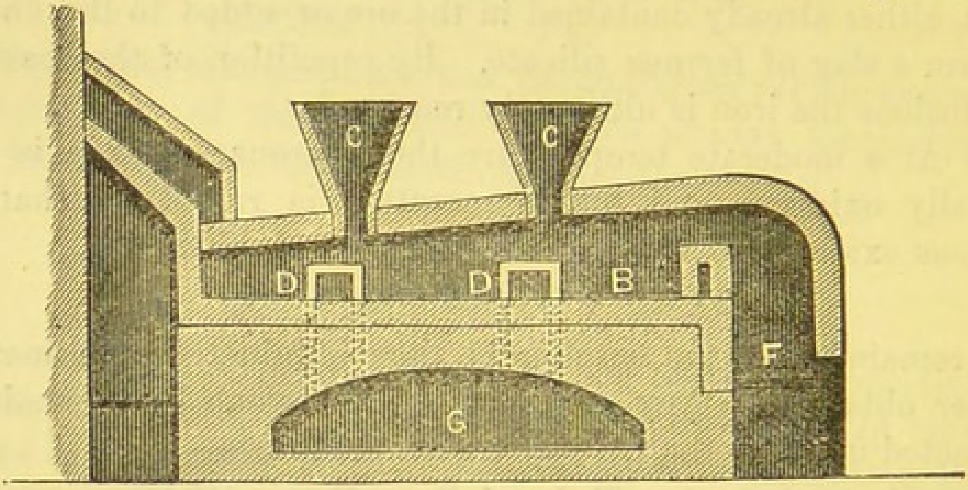


FIG. 33.

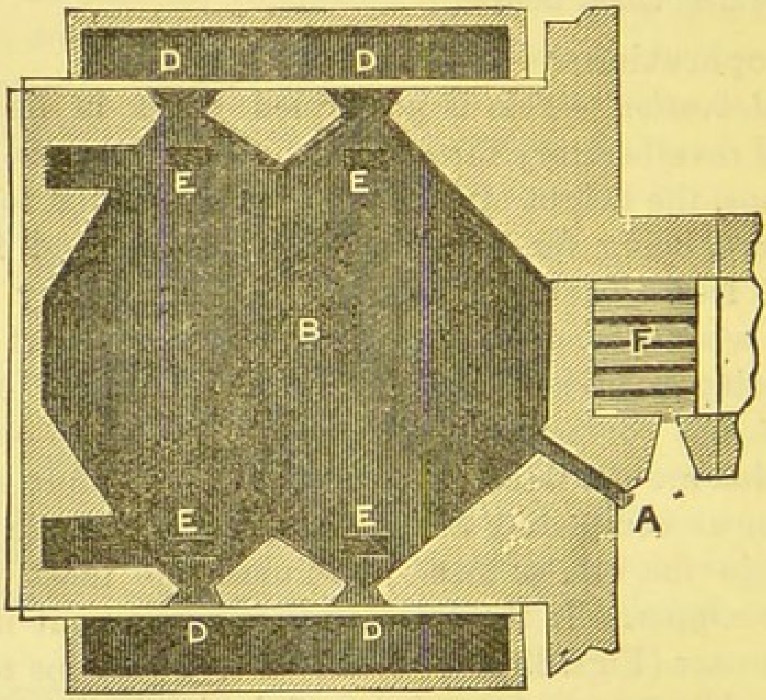


FIG. 34.

somewhat like the above, but whose grate area in proportion to the furnace bed is larger, viz. about 1 to 5. At this stage, ferrous oxide forms by double decomposition between ferrous sulphide and cuprous oxide, and this combines with silica, forming the slag, ferrous and lime silicate, whilst the cuprous sulphide, and the ferrous sulphide still remaining, form the *regulus* or *coarse metal.* The slag contains very little copper and is run off and thrown away; the regulus consists of about equal proportions of cuprous and ferrous sulphide.

3. The coarse metal is now brought into a fine state of division by running it hot from the furnace into water, and the calcining and fusing operations are repeated in order to remove the rest of the iron as completely as possible. The product obtained is termed *white metal*, and consists essentially of cuprous sulphide.

4. *The roasting.*—The object of this operation is to partially oxidize the cuprous sulphide and to induce the rest of the iron and other impurities to form a slag. It is performed in a reverberatory furnace with a fire grate still smaller than that used in the calcination stage and an increased air supply. When the oxidation has proceeded far enough, the temperature is raised so as to bring about the reaction between the cuprous oxide and the sulphide.

5. *The refining.*—The crude copper ("blister copper") is fused in an oxidizing atmosphere on the bed of the refining furnace and impurities such as arsenic, sulphur, iron, antimony, etc., still remaining, are oxidized and skimmed off as a slag. Finally anthracite is sprinkled on the surface of the molten metal and agitation and admixture promoted by stirring the mass with "green" poles of wood. In this way the reduction of any remaining cuprous oxide is effected and particles of slag are carried to the surface.

On the continent it is now very usual to calcine the ore to the oxide, and then effect the reduction with coke in a form of blast furnace.

The electrolytic process.— This process, although sometimes applied for the purpose of obtaining copper from the "white metal," or even from the ore, is usually only adopted for the removal of the impurities from crude copper resulting from metallurgical operations. Ingots of copper are suspended in a tank or series of tanks containing a solution of sulphate of copper to which sulphuric acid is added. These constitute the anodes, and the kathodes on which, during the passage of the current, the pure copper deposits, consist of thin sheet copper. The impurities pass into solution with the exception of the silver and gold, which collect as a slime at the bottom of the tank. By this method therefore it is possible not only to obtain copper of a very high degree of purity but also to recover the silver and gold.

Extraction of copper from burnt pyrites.—Most of the pyrites now used as a source of sulphur in the manufacture of sulphuric acid contains from 3 to four per cent of copper. The burnt pyrites is ground and intimately mixed with from 10 to 20 per cent. of its weight of salt, and then roasted in a reverberatory furnace so as to obtain the iron as far as possible in the form of ferric oxide, the copper being left chiefly as cupric chloride. The product is then lixivated with water to extract the copper salts, and the deposition of the copper effected by means of scrap iron.

Properties of metallic copper.—The metal has a red colour by reflected light and in thin plates it transmits green light. Its specific gravity is 8·95 ; when heated and allowed to cool slowly it is brittle, but if cooled rapidly it is much softer and highly malleable and ductile. With the exception of silver, it is the best conductor of heat and electricity known. It possesses considerable tenacity, but this falls off rapidly when it is heated ; at about 1050° C. it melts, and at very high temperatures it may even be distilled. Dry air is without action upon it, at ordinary temperatures, but in presence of moisture and carbon dioxide it becomes corroded and coated with a deposit of basic carbonate. Hydrochloric and sulphuric acid have very little action upon it ; the latter however undergoes decomposition when heated in contact with copper, sulphur dioxide being evolved ; nitric acid if somewhat diluted with water is readily acted upon, with the formation of nitrate of copper and nitric oxide.

Alloys.—With zinc it forms brass, and with tin, bell metal, gun metal, speculum metal and bronze, the latter often containing also zinc or lead.

The oxides and hydroxide.—The lower oxide, *cuprous oxide* Cu_2O, occurs native as cuprite, a mineral which crystallizes in octahedra. It is also found amongst the products obtained in the extraction of copper in deep red opaque masses. If to solutions of copper salts, potash be added (in presence of an alkaline tartrate, to prevent the precipitation of the hydroxide) and then a reducing agent such as grape sugar, a reddish-yellow precipitate of cuprous oxide is obtained. This dissolves in ammonia, forming a colourless solution. The solutions of cuprous salts are in general colourless, but they are very unstable and rapidly absorb oxygen from the air and turn blue, owing to their transformation into cupric salts.

Cupric oxide, CuO, is a black oxide obtained by oxidation of the metal or by heating the hydroxide, carbonate or nitrate. At high temperatures it loses oxygen and is converted into the cuprous oxide or a lower oxide Cu_3O. Hydrogen, carbonic oxide or other reducing agents undergo oxidation in contact with heated cupric oxide, and it is therefore used in the analysis of organic substances, the carbon and hydrogen of which are converted into carbon dioxide and water respectively. Cupric oxide dissolves in molten glass, imparting a green colour to it, whilst cuprous oxide gives it a ruby-red tint.

The *hydroxide*, $Cu(OH)_2$, is obtained as a greenish bulky precipitate, when caustic potash is added to cupric salts in the cold. On boiling, the precipitate turns black, since at moderate temperatures the hydroxide gives up water and is converted into the black cupric oxide. It dissolves in ammonia to a deep blue solution which has the property of dissolving cellulose (filter paper).

Cuprous sulphide, Cu_2S, is the "white metal" obtained in the metallurgy of copper; it may be prepared by exposing finely divided copper or copper foil to sulphur vapour. It crystallizes both in the regular and rhombic system and is isodimorphous with the corresponding sulphide of silver, with which it often occurs associated in the mineral kingdom.

Cupric sulphide, CuS, is the dark-brown precipitate obtained when copper salts are precipitated by sulphuretted hydrogen. When exposed to air in the moist condition it gradually oxidizes to cupric sulphate, and if heated in the dry condition readily passes into cuprous sulphide.

Copper forms also two series of haloid salts, the cuprous Cu_2F_2,

Cu_2Cl_2, etc., and the cupric CuF_2, $CuCl_2$, etc. These haloid salts, though in general tolerably stable in solution and obtainable therefrom on concentration in crystals, are readily decomposed by heat and converted into the cuprous form, in which they are insoluble in water. The cupric iodide however breaks up even in the moist condition, and the precipitate obtained on adding potassium iodide to solutions of cupric salts consists of white cuprous iodide and iodine. Cuprous salts give under the same circumstances a pure white precipitate of cuprous iodide.

Cuprous chloride, Cu_2Cl_2, is formed by burning copper in chlorine or by the action of reducing agents such as stannous chloride, $SnCl_2$, zinc dust or metallic copper on the cupric chloride. If therefore cupric oxide be dissolved in concentrated hydrochloric acid, the solution when boiled with excess of copper contains cuprous chloride which is deposited as a white powder when it is poured into a large quantity of water. This, on exposure to air, turns green owing to the formation of a basic chloride. The solution of cuprous chloride in ammonia absorbs carbonic oxide and is used for determining the amount of this gas in certain gaseous mixtures; in presence of acetylene, C_2H_2, a basic cuprous acetylide is formed from which pure acetylene may be liberated by treatment with acid.

Cupric chloride, $CuCl_2$, is formed when copper or the cuprous chloride is heated in excess of chlorine. It is a brown deliquescent powder. It is obtained as a yellow solution by digesting cupric oxide with concentrated hydrochloric acid, and this when placed in a freezing mixture deposits red needles of the composition $HCl.CuCl_2.3H_2O$. The colour of the solution changes on dilution, becoming first green and then blue. Several oxychlorides are known, one of which is the product obtained by the action of a small quantity of bleaching powder on a solution of cupric sulphate; it is used as the pigment Brunswick green.

The haloid salts of copper show a marked tendency to combine with ammonia and with the haloid salts of the alkalies. The more important of such compounds are—

(1) $Cu_2Cl_2.2NH_3$ and $CuCl_2.4NH_3$ obtained by dissolving cuprous and cupric chlorides respectively in a solution of

ammonia; the former is on concentration deposited as white crystals and the latter as dark blue.

(2) $2NH_4Cl.CuCl_2.2H_2O$ and $2KCl.CuCl_2.2H_2O$ which are formed when ammonium chloride and potassium chloride are respectively mixed, in concentrated solution, with cupric chloride.

The **cyanides** of copper bear a considerable resemblance to the chlorides. The double cyanide of potassium and copper is soluble in water and is not decomposed by the action of sulphuretted hydrogen. The corresponding double cyanide of cadmium is decomposed under these circumstances. Hence if copper and cadmium be both present in this form, sulphuretted hydrogen may be used for their separation, cadmium only being precipitated as sulphide.

Copper resembles the alkalies in forming a chlorate, bromate, iodate and perchlorate, but these bodies do not possess any considerable stability.

Cupric sulphate, $CuSO_4$.—This salt may be obtained in the form of blue triclinic crystals of the composition $CuSO_4.5H_2O$ by dissolving cupric oxide in sulphuric acid and allowing the solution to crystallize. By gently heating, these crystals lose water and are converted into anhydrous cupric sulphate, a white powder which readily takes up moisture from the air and may be used as a desiccating agent. The hydrated salt is readily soluble in water, but, as in other cases, when it is in the anhydrous form it is less soluble; 100 parts of water dissolve at—

	0°	20°	40°	60°	80°	100°
$CuSO_4.5H_2O$	31·6	42·3	56·9	77·4	118·0	203·3
$CuSO_4$	18·2	23·5	30·3	38·8	53·1	75·3

Cupric sulphate is known in commerce under the name *blue vitriol*, the corresponding zinc salt being *white vitriol* and the iron salt *green vitriol*. It is largely used for the preparation of other copper salts and in solution is employed as a bath for the electrolytic deposition of copper. By digestion with copper hydroxide several basic sulphates may be obtained, *e. g.* $2CuO.CuSO_4$ and $3CuO.CuSO_4$. When excess of ammonia is added to a solution of sulphate of copper, the precipitate which first forms redissolves to a deep blue solution, from which purple rhombic prisms having the composition $CuSO_4.(NH_3)_4H_2O$ separate out, and this on being heated to 150° C. yields a green powder $Cu(NH_3)_2SO_4$. Copper also forms a selenate, $CuSeO_4.5H_2O$, resembling the sulphate and isomorphous with it.

The *nitrates and phosphates* of copper are of lesser importance. *Basic carbonates* only are known; they are usually prepared by the action of the alkaline carbonates on sulphate of copper. Like the *silicates* they are best known as the minerals malachite $CuCO_3.Cu(OH)_2$ azurite, $2CuCO_3.Cu(OH)_2$, dioptase $CuSiO_3.H_2O$ and chrysocolla $CuSiO_3.2H_2O$.

Detection and estimation.—Copper compounds give a bluish-green or emerald-green colour to the Bunsen flame; the spectrum is a complex one consisting of a large number of lines and fluted bands, those in the green being especially well marked. When fused with borax, the mass is green when hot and blue on cooling; by reduction, especially in presence of tin, a beautiful ruby tint is obtained. Copper compounds are easily reduced on charcoal to the metallic condition. They are precipitated by sulphuretted hydrogen as cupric sulphide insoluble in dilute mineral acids.

The estimation is usually made in the form of oxide, the hydroxide being precipitated by means of caustic soda and converted into the black oxide by boiling. A second method, which in some cases is convenient, consists in the deposition of metallic copper either by immersion of iron in the solution or electrolytically.

SILVER.

Occurrence.—The chief natural forms are metallic silver, silver glance, Ag_2S, stephanite $5Ag_2S.Sb_2S_3$, ruby silver ore consisting of sulphides of silver and antimony or silver and arsenic, horn silver $AgCl$. Much silver is also extracted from galena. (See p. 240.)

Extraction of silver.—

1. *By amalgamation.*—Several methods have been described depending on the action of mercury on silver compounds, whereby the silver is dissolved in the mercury, the mercury being separated ultimately from it by distillation. These methods are historically interesting and the details as now mostly

employed being as follow. The ore is finely powdered and mixed into a slime with water; it is then brought into intimate contact with about $\frac{1}{10}$ its weight of mercury for two or three hours and the amalgam separated as completely as possible from the mud in settlers. This amalgam consists of (*a*) solid amalgam containing much silver and (*b*) liquid amalgam which is the excess of mercury containing small quantities of silver. The solid amalgam is submitted at once to distillation whilst the liquid is used again in the amalgamation process. In some ores a previous roasting with common salt is desirable in order to convert the silver into a form in which it is readily acted upon by mercury.

2. *By wet processes.*—The ore is preferably transformed first into the chloride by roasting it with common salt, and this chloride is then dissolved out with brine or with sodium thiosulphate and the silver finally precipitated as sulphide by the addition of sodium sulphide. The silver sulphide is then calcined in a reverberatory furnace. In the "Ziervogel" process the sulphide is roasted to sulphate, but as the ore contains usually iron, copper and lead, these are also transformed by roasting, into sulphates. If the mixed sulphates be then exposed on the bed of the furnace to a higher temperature, the sulphates of iron and copper are decomposed before the silver sulphate. This latter is then extracted by water and metallic silver precipitated therefrom by means of scrap copper.

3. *The desilverizing of lead.*—About one-third of the silver produced is extracted from lead; the methods used will be described under that metal. (See page 240.)

Pure silver is a white metal, lustrous, and capable of taking a high polish and of being hammered or rolled into plate and drawn into wire. These properties of malleability and ductility it possesses in almost as high a degree as gold, so that silver sheet $\frac{1}{10000}$ of an inch thick and wire $\frac{1}{3000}$ of an inch thick may be obtained; its tensile strength is over 17 tons to the square inch of section. Its specific gravity, like that of other metals, varies somewhat according to the treatment to which it is subjected, being about 10·3 to 10·6 in the solid condition and 9·46 in the molten state. It melts at 954° C. and may be distilled at the highest temperature of the oxyhydrogen blow-pipe. It is a better conductor of heat and electricity than even copper. By the action of certain reducing agents on silver salts the metal is obtained in a finely divided condition, in which form it shows brilliant golden, ruby, blue and other tints.

The oxides and hydroxides.—The hydroxide is obtained as a brown powder by adding caustic potash to solutions of silver salts. It is an unstable body and above 100° C. it gradually loses water and passes into the *oxide* Ag_2O, which also decomposes into metallic silver and oxygen at about 300° C. It dissolves in ammonia, and on exposure of the solution to air *fulminating silver* separates out. This body detonates on the slightest friction when it is dry and sometimes even in the moist state. It seems to have the composition Ag_3N. When a solution of silver nitrate is electrolyzed, black needles form on the kathode; these vary in composition according to the circumstances under which they are obtained, but give evidence of containing an unstable *peroxide* of silver, Ag_2O_2.

Silver Sulphide, Ag_2S, is obtained either by heating together silver and sulphur or by precipitating silver salts with sulphuretted hydrogen. This compound and also corresponding compounds with selenium and tellurium are found as minerals.

Silver fluoride, AgF, is formed when the oxide or carbonate is dissolved in hydrofluoric acid. It crystallizes from water as $AgF.H_2O$ or $AgF.2H_2O$. It is soluble in little more half its weight of water, the solution having a strongly alkaline reaction. The salt takes up about 840 times its volume of ammonia.

Silver chloride, AgCl.—This salt is obtained as a white curdy precipitate when hydrochloric acid or a soluble chloride is added to silver salts. Like the bromide of silver it is affected by exposure to sunlight or other chemically active rays; it assumes at first a violet tinge, ultimately dark brown, and undergoes loss of chlorine. Though insoluble in water, and practically so in mineral acids, silver chloride dissolves readily in ammonia, in solutions of sodium sulphite, or thiosulphate and in potassium cyanide. It dissolves also somewhat easily in alkaline chlorides, and salt brine is frequently used for the extraction of silver. The precipitated chloride absorbs ammonia and forms $2AgCl.3NH_3$, and a similar body separates out of a saturated solution of silver chloride in ammonia in octahedral crystals. The chloride is reduced to metallic silver by the action of zinc in presence of dilute sulphuric acid, by heating it in a current of hydrogen or by fusion with alkaline carbonates or in presence of organic substances.

The *bromide*, $AgBr$, and *iodide*, AgI, are both found native in Mexico and Chili. The bromide dissolves in ammonia, though less freely than the chloride, and the iodide is almost insoluble in ammonia. The iodide is nearly insoluble in alkaline chlorides, and hence, when salt brine is used for the extraction of silver, the silver iodide may be thrown down by the addition of a soluble iodide. Though insoluble in a solution of ammonia, the dry iodide takes up large quantities of gaseous ammonia, forming $2AgI.NH_3$.

Silver cyanide, $AgCy$, is obtained by adding a soluble cyanide to a solution of silver nitrate. It resembles the chloride in most respects. Ammonia and the alkaline cyanides dissolve it. If potassium cyanide be added to silver nitrate solution until the precipitate which first forms is just redissolved, the solution on concentration yields the double cyanide $KCy.AgCy$. A solution of this salt is employed in electroplating.

Silver hypochlorite, $AgClO$.—In regard to the similarities which are observed between the salts of silver and those of the alkalies, it is of interest to point to the existence of a series of compounds derived from the oxyacids of chlorine. The hypochlorite is obtained by agitating excess of the hydroxide or carbonate in water containing chlorine ; this however soon undergoes rearrangement and becomes transformed into the *chlorate* (soluble in water) together with the *chloride*, especially if the chlorine is used in excess. *Bromate* and *iodate* of silver, which are almost insoluble in water, have been prepared by double decomposition of silver salts with soluble iodates. The *perchlorate*, $AgClO_4$, is obtained by dissolving silver oxide in perchloric acid ; it is soluble in water, and in the absence of organic matter is a tolerably stable body.

Silver sulphate, Ag_2SO_4, is formed by dissolving the oxide or carbonate in sulphuric acid. It dissolves in about 200 times its weight of cold water, but is much more soluble in hot. It crystallizes in rhombic prisms, and is isomorphous with sodium sulphate. The existence of a silver hydrogen sulphate, $AgHSO_4$, a silver alum, $Ag_2SO_4.Al_2(SO_4)_3.24\,H_2O$, and an octosulphate, $Ag_2O(SO_3)_8$, further exhibit the relationship of silver with the alkalies. Silver sulphate, like copper sulphate, forms a compound with ammonia, of the composition $Ag_2(NH_3)_2SO_4$.

Silver nitrate, $AgNO_3$, is obtained by dissolving the metal in nitric acid. It readily dissolves in water, and is the form in which silver is most frequently employed as a reagent. It possesses a powerful corrosive action on organic tissues, which are stained black by it; it acts also similarly on vegetable fibre, and is used as the basis of many preparations of "marking ink." Dry silver nitrate absorbs ammonia, forming $AgNO_3.2\,NH_3$; it also forms double salts with nitrates of the alkalies, *e. g.* $KNO_3.AgNO_3$, $NH_4NO_3.AgNO_3$, these being formed as crystals by bringing together solutions of the respective nitrates, and allowing them slowly to evaporate.

The phosphate, Ag_3PO_4, is a light yellow powder, and the *arsenate,* Ag_3AsO_4, a brick-red powder which serve as means of recognizing the presence of phosphoric and arsenic acids or their salts.

Silver carbonate, Ag_2CO_3, is an unstable white powder, obtained by precipitating silver nitrate with an alkaline carbonate. If silver nitrate be treated with potassium carbonate in presence of carbon dioxide, $AgKCO_3$ is obtained.

Detection and estimation.—Silver is separated from most other bodies by reason of the insolubility of the chloride in water and acids, and its solubility in ammonia.

Its compounds are readily reduced by being heated on charcoal, and the residue of metallic silver is easily recognized. The quantitative estimation is usually made in the form of chloride, with the precaution that alkaline chlorides or hydrochloric acid shall not be present in excess, since silver chloride is soluble in these reagents.

GOLD.

Occurrence.—Gold is almost always found in the metallic condition, usually associated however with certain quantities of silver, copper, or iron, and also in special ores bismuth and tellurium occur. Many minerals, such as galena, iron pyrites and zinc blende, contain traces of gold. Though one of the rarest of metals, it is widely distributed; the chief localities where it is mined being in Australia, California, or South Africa. The metal is extracted either from quartz veins, or from deposits of alluvial gravel; and partly in consequence of the value of the metal, partly from the simplicity of the methods by which it is worked, a deposit containing as little as 1 part of gold in 500,000 may sometimes be profitably worked. The gold quartz is first powdered roughly by mechanical means, and then subjected to levigation in sluices, so arranged that the heavier particles containing the gold collect at the bottom of the sluice, whilst the gangue is carried off by the stream of water. The gold is separated by causing it to form an amalgam with mercury, or to collect on amalgamated copper plates. The mercury is finally distilled off, leaving the gold behind as a residue.

In the *chlorination process* the ore (iron pyrites) is roasted, so that the iron is transformed into ferric oxide, which is not readily attacked by moist chlorine, and then subjected to the action of chlorine. The gold is thus converted into chloride, which can be dissolved out in water, and metallic gold precipitated from the solution by the addition of reducing agents, such as ferrous sulphate. Potassium cyanide is now largely used for extracting gold, as it readily dissolves in this reagent.

The separation of silver and copper from gold may be effected by "quartation," the success of which, as the name implies, depends on the gold being present to the extent of not more than one quarter of the mass of metal employed. The metal is boiled with strong sulphuric acid, and the silver and copper are thus converted into sulphates, so that on lixivation with water these are dissolved and the gold left as a residue.

In masses of the metal the characteristic colour and lustre of gold is shown; but if it be precipitated in a fine state of division by means of ferrous sulphate or phosphorus, it has a blue or purple tint by transmitted light, and a reddish brown colour by reflected light. Gold leaf in transmitted light appears of a green or blue colour. Its characteristic features are its great malleability and ductility, and its resistance to oxidation and to the action of acids. Gold leaf may be obtained so thin that 250,000 sheets occupy the thickness of one inch. It is insoluble in any single mineral acid, but readily dissolves in "aqua regia," which consists of a mixture of hydrochloric acid with nitric acid.

Gold has a tensile strength of 7 tons to the square inch, and a specific gravity of 19·3; it melts at about 1040° C. Its alloys with copper and silver are important. Copper heightens the colour of gold, and silver renders it paler, whilst the alloy is invariably harder and more durable than pure gold.

Purple of Cassius is a fine purple precipitate obtained by adding a solution of stannous chloride, containing stannic chloride, to the chloride of gold. Its composition is variable, but it consists essentially of gold associated with oxide of tin, and is used for the obtaining a fine ruby tint in glass, enamel or porcelain.

The oxides.—Although gold does not combine directly with oxygen, oxides may be obtained by the action of caustic alkalies on salts of gold. Aurous chloride, $AuCl$, yields *aurous oxide*, Au_2O, and auric chloride, $AuCl_3$, under certain conditions gives *auric oxide*, Au_2O_3. These oxides are however very unstable, and difficult to prepare in a state of purity. By the action of strong ammonia on aurous oxide, a black explosive body, having the composition $Au_3N.NH_3$, is formed, and this, when boiled with dilute acids, forms the nitride Au_3N.

The auric oxide dissolves readily in alkalies, and forms *aurates;* potassium aurate is soluble in water, and is used in the deposition of gold in electro-gilding.

Of the **haloid salts** the most important is the *auric chloride*, $AuCl_3$, obtained when the metal is dissolved in aqua regia; from a moderately concentrated solution of this salt, yellow needles separate out having the composition $HAuCl_4$, and in presence of alkaline chlorides, double salts (*e. g.* $KAuCl_4$) derived from this acid may be prepared. On heating the auric chloride to 180° C., it loses chlorine and is converted into *aurous chloride*. Both salts however are unstable, and at a moderate temperature are entirely decomposed. Bromine, iodine, and cyanogen compounds exist; these resemble the chlorides and like them form double salts with the haloid salts of the alkalies.

Gold does not unite directly with sulphur, but by passing sulphuretted hydrogen through a solution of the double salt of gold and potassium cyanide, KCy.AuCy, *aurous sulphide*, Au_2S, is precipitated, and from a dilute solution of the trichloride the *disulphide*, Au_2S_2, is precipitated. These sulphides are soluble in alkaline sulphides with which they form soluble double salts.

Detection and estimation.—Gold is thrown down from its solutions by sulphuretted hydrogen, the precipitate being soluble in ammonium sulphide or alkaline sulphides. The formation of purple of Cassius (see above) affords a delicate test for the presence of gold. Ferrous sulphate precipitates metallic gold from its solutions, and this shows the characteristic colour and lustre of gold when it is burnished in an agate mortar. The metal is also readily obtained by heating a salt of gold on charcoal. It is always estimated in the form of the metal, its compounds being all unstable and difficult to prepare in a state of purity.

PLATINUM.

Occurrence.—This element invariably occurs in the free state, associated with the metals ruthenium rhodium, palladium, osmium, and iridium. The chief localities where it is found are the Ural mountains, New Granada, Brazil, California, and Australia.

In order to separate the platinum the ore is digested with aqua regia, osmium and iridium remain undissolved whilst the other metals pass into solution. Palladium is separated in the form of $(PdCy)_2$ by adding a solution of mercuric cyanide to the solution containing the metals. The platinum is next precipitated as $(NH_4)_2PtCl_6$ on addition of ammonium chloride. When the ammonium platinic chloride is heated to redness it decomposes, leaving the metal in the form known as *spongy platinum.*

Properties of platinum.—The metal is readily obtained from its compounds by the action of reducing agents or by heat alone. It possesses small chemical affinity for other elements and forms unstable compounds. It has a grey colour when in mass, and is malleable and ductile in a marked degree, and of high specific gravity (about 22). Platinum fuses only at a very high temperature, but can be welded at a red heat, in a finely divided state the metal has the property of absorbing 100 times its volume of oxygen and 110 volumes of hydrogen, in this form the metal is an active medium in promoting certain chemical changes, thus the union of oxygen and hydrogen is brought about with explosive violence; a jet of hydrogen directed upon finely divided platinum causes the metal to glow and the gas becomes ignited. Platinum is not acted on by either nitric or hydrochloric acid alone, but is dissolved by aqua regia.

Oxides and hydroxides.—Platinum forms two oxides, PtO and PtO_2, these are obtained by heating the corresponding hydroxides $Pt(HO)_2$ and $Pt(HO)_4$.

Platinum tetrachloride, $PtCl_4$.—This compound is much used as a reagent in quantitative estimations, it can be obtained in a pure state by the following method. Dissolve some of the commercial platinum in aqua regia and evaporate the solution to dryness to get rid of excess of acid: dissolve the residue in water. To the solution (only slightly acid) add caustic soda till alkaline, and boil for some minutes; all the chlorides of the platinum metals, *except that of platinum itself*, are reduced to lower chlorides, *e.g.*, with palladium.

$$PdCl_4 + 2\ NaOH = PdCl_2 + NaCl + NaClO + H_2O.$$

Now add a little alcohol, and boil again in order to reduce the sodium hypochlorite and prevent it transforming the lower chlorides back again to the higher form. We have now present as *tetrachloride*, only platinum, and when ammonium chloride is added only platinum will be precipitated as (Am_2PtCl_6), since the ammonium salts of the lower chlorides are all soluble. On igniting the Am_2PtCl_6 pure platinum will be obtained, and may be dissolved by boiling with hydrochloric acid to which a drop of nitric acid is added from time to time.

Platinum tetrachloride is a dark brown deliquescent salt which readily dissolves in water, alcohol and ether. When a mixture of $PtCl_4$ and HCl is allowed to evaporate over sulphuric acid, brown red crystals of chloro-platinic acid are obtained, having the composition $H_2PtCl_6 . 6 H_2O$. When this compound is heated to a temperature of 235° C it breaks up into hydrochloric acid and $PtCl_4$. Platinum tetrachloride forms double salts with the chlorides of the alkali metals, having the formula K_2PtCl_6. $(NH_4)_2PtCl_6$, and Na_2PtCl_6; the first two are insoluble, whilst the last is readily soluble in water and in alcohol. $PtCl_4$ is used for separating potassium and ammonium from sodium in analysis.

Platinous chloride, $PtCl_2$.—This is obtained by heating platinic chloride to a temperature of about 200° as long as chlorine is evolved, or by reducing platinic chloride (in solution) with SO_2. It is a green coloured compound insoluble in water. It forms double salts with the chlorides of the alkali metals, for example, 2 KCl, $PtCl_2$.

Ammonia bases.—Although platinum forms no nitride it yields a very peculiar class of ammonia derivatives, consisting of strongly basic hydroxides and salts of these. The hydroxides are such powerful bases that they compare with the caustic alkalies, and will expel ammonia from ammonium salts, absorb carbon dioxide from the air, precipitate the hydroxide of aluminium (also $Fe_2(HO)_6$, etc.), the precipitate being soluble in excess, just as it is with caustic potash or soda. The salts and bases are very numerous, we can only mention some of the best known of the series.

If $PtCl_2$ be dissolved in hydrochloric acid and ammonia be added to the boiling solution, brilliant green crystals are deposited on cooling, having the composition $Pt(NH_3)_4Cl_2.PtCl_2$ (green salt of magnus), and by boiling this for some time with ammonia it ultimately dissolves, and from the solution alcohol will precipitate Reiset's first chloride, $Pt(NH_3)_4Cl_2$. If this chloride be heated to 250° C so long as ammonia is evolved we obtain Reiset's second chloride, $Pt(NH_3)_2Cl_2$. These chlorides may be transformed into sulphates by the action of sulphuric acid, and by adding just sufficient baryta water to combine with the sulphuric acid the free base is obtained.

The following equations illustrate the changes which occur :—

(1) $Pt(NH_3)_4Cl_2 + H_2SO_4 = Pt(NH_3)_4SO_4 + 2 HCl$

and $Pt(NH_3)_4SO_4 + Ba(OH)_2 = Pt(NH_3)_4(OH)_2 + BaSO_4$

(2) $Pt(NH_3)_2Cl_2 + H_2SO_4 = Pt(NH_3)_2SO_4 + 2 HCl$

and $Pt(NH_3)_2SO_4 + Ba(OH)_2 = Pt(NH_3)_2(OH)_2 + BaSO_4$.

CHAPTER XIII.

THE IRON GROUP.

Fe, Co, Ni.

General Characters.—

1. Iron, like cobalt and nickel, occurs in the mineral form in combination with sulphur and arsenic; the three metals frequently replace one another in the same ore and the crystals are isomorphous—*e. g.* mispickel, FeSAs, nickel glance, NiSAs, cobalt glance, (FeCo)AsS, speiss-cobalt, $(FeCoNi)As_2$.

2. The metals are difficult to fuse, Ni being most fusible and Fe least fusible, just as occurs in the platinum group.

Approximate melting point in degrees Centigrade—

Iron.	Cobalt.	Nickel.
1800	1800	1600
Ruthenium.	Rhodium	Palladium.
1800	2000	1500
Osmium.	Iridium.	Platinum.
2500	1950	1780

Iron and cobalt decompose water at a red heat, but in the case of nickel the decomposition proceeds less readily.

The metals are magnetic but lose this property when strongly heated; iron at 780° C., cobalt at a higher temperature than this, and nickel at a still higher temperature than cobalt.

They also occlude hydrogen, nickel (just as its analogues Pd. and Pt. do in the platinum group) in the highest degree.

3. The oxides and chlorides are most stable in the case of iron and least so in the case of nickel—*e. g.* Fe_2Cl_6 can be volatilized without decomposition, Co_2Cl_6 is extremely unstable,

whilst with nickel no higher chloride than $NiCl_2$ has been obtained.

4. The double cyanides show similar behaviour.

K_4FeCy_6 stable, K_4CoCy_6 moderately stable
K_3FeCy_6 ,, K_3CoCy_6 stable

But in the case of nickel no such double cyanides have been obtained, the only salt of this type being K_2NiCy_4

IRON.

Occurrence.—In the *metallic* form iron has been found in large masses in Greenland and occurs also in meteorites associated with cobalt and nickel. As *oxides* it is found as magnetite, Fe_3O_4, in masses or octahedral crystals chiefly in Lapland, Sweden, Siberia, and some parts of North America; as hæmatite, Fe_2O_3, in Belgium, Sweden, Elba, on the south of Lake Superior, and in England it is worked in the neighbourhood of Whitehaven and Ulverston; as limonite, $2Fe_2O_3.3H_2O$, in South Wales and in Spain; the bog iron ores which occur in Ireland, Sweden and North Germany belong to the class of hydrated oxides. The *carbonate* is known as the mineral spathic iron ore, or in the less pure and more earthy form of clay ironstone, and associated with carbonaceous matter, as black band ironstone. As *sulphides* there is iron pyrites, FeS_2, occurring in large quantities in Spain, and crystallizing in the regular system, the form known as marcasite crystallizing in the rhombic system.—The principal arsenical iron ore is mispickel, FeSAs.

Metal.—The ores employed in the production of iron on the large scale must be such as can be readily reduced and contain as little arsenic and sulphur as possible, since these elements are difficult to eliminate and have a deteriorating effect on the metal. The oxides or hydrated oxides and carbonates are the only ores which are applicable to iron smelting.

Production of pig iron.—The ore (if clay ironstone or a spathic ore) is first calcined and then subjected to the operation of smelting in a blast furnace.

The *calcination* is performed by stacking the ore, along with a small quantity of fuel, in heaps (or in shallow kilns), and carefully regulating the temperature and air supply so that—

(*a*) Most of the moisture, carbon dioxide, sulphur and arsenic are expelled.

(*b*) The ferrous oxide undergoes sufficient oxidation to ferric oxide to avoid the production of ferrous silicate during the smelting operation.

(*c*) The ore is rendered more porous, a condition which facilitates its ultimate reduction to metallic iron.

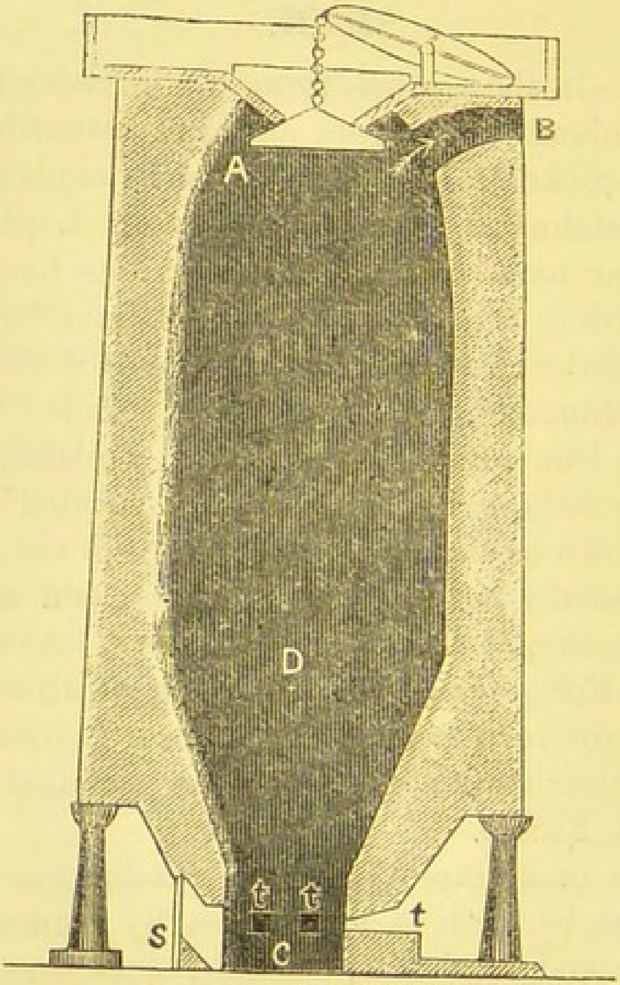


FIG. 35.

The calcining operation is thus not only essential for getting rid of certain objectionable impurities but also relieves the work of the blast furnace.

The *smelting* is performed in a tall furnace known as the blast furnace, the form of which will be seen by reference to Fig. 35. The height of such a furnace may be as much as 80ft. and its greatest internal width 25ft. (viz. at the "boshes" D). The mouth of the furnace is closed by a "cup and cone," as shown at A, and the waste gases arising from it pass away by a pipe which is shown at B, just below the mouth. In its lower part the furnace gradually narrows below the boshes and at its base is the "hearth" C, a space about 8ft. in diameter and the same in height.

There is an outlet for the slag at S, just above the "dam" in the "fore hearth," which is shown in the figure just to the left of the hearth proper. Below this, the iron is tapped off at intervals of about 12 hours. The charge in such a furnace consists of 4 parts calcined ironstone to 1 part of limestone with coke equal to somewhat less than half the weight of the ironstone, though the proportions vary in some degree according to circumstances, such as the nature of the ore, and the character of the pig-iron to be produced. The air is introduced under forced blast at openings, near the base of the furnace, by water-jacketed twyers, 5 tons (or about 5000 cubic yards) of air, and 2½ tons of calcined ore being required per ton of iron produced.

This quantity of air, large as it seems, is insufficient for the complete oxidation of the carbon and the gases escaping from the furnace consist chiefly of carbon monoxide and nitrogen. They are led off by the pipe previously referred to and furnish the means of heating the air supplied to the furnace ; this effects an economy of fuel and also conduces to the attainment of a high and equable temperature in the furnace. The process goes on continuously for years, until indeed the furnace must be blown out for repairs, and fresh quantities of the charge are periodically introduced by lowering the cone at the mouth of the furnace.

The temperature and the composition of the materials in the furnace of course vary at different parts. The temperature of the charge in the upper zone does not exceed dull red-heat, and lower down increases until near the base of the furnace a white heat (over 2000° C.) prevails. The charge becomes gradually heated up in the upper zone, and lower down is reduced in the atmosphere of carbon monoxide (and nitrogen), but the iron remains in the spongy condition, the temperature being insufficient to melt it ; the charge slowly descends and at the lower parts of the furnace it takes up carbon in considerable quantity, melts and collects on the hearth of the furnace. About midway, the limestone is decomposed into lime and carbon dioxide, and as the narrower part of the furnace is reached, the lime combines with siliceous matters, forming a molten slag, which being specifically lighter, collects above the iron and flows off, as the process goes on, at the slag hole. When a sufficient amount of metal has accumulated, it is run off and cast in open furrows of sand in "pigs."

White pig is fine grained and contains 3 to 4 per cent. of carbon, chiefly in the form known as "combined" carbon; if treated with dilute hydrochloric acid it dissolves almost completely, evolving gaseous hydrocarbons. *Grey pig* is coarse grained, and when freshly fractured, crystals of graphite are visible to the naked eye; the amount of carbon present does not differ essentially from that in white pig, but it is chiefly in the graphitic form and is not acted upon by dilute acid. Such pig iron when heated with dilute acid leaves therefore a residue consisting of carbon. There is also an intermediate form known as "*Mottled pig.*" In addition to carbon, pig iron contains smaller quantities of silicon (about 2 per cent.), phosphorus (about 0·7 per cent.), and sulphur (about 0·1 per cent.).

Production of wrought iron.—Wrought iron as a commercial product is essentially iron containing only a minimum quantity of such impurities, amounting in all to about 0·5 per cent. The removal of carbon, sulphur, etc. is effected by first "puddling" the pig iron, a process in which the latter is heated in contact with ferric oxide in presence of air and then hammering and rolling it whilst hot, the mechanical pressure serving to develop a fibrous texture and to squeeze out slag and other matters retained by the iron.

Production of steel.—Steel consists of iron associated with from 0·15 to 1·15 per cent. of carbon. The processes mostly employed for making steel are (*a*) the cementation process; (*b*) the Bessemer process; (*c*) the Siemens-Martin process.

Cementation consists in heating wrought iron bars for some days (usually 1 to 2 weeks) in contact with charcoal or carbonaceous matter; the bar gradually takes up carbon, the outer portions being more fully carbonized than the inner. To secure uniformity of texture and composition, the product is melted and subjected to rolling and hammering.

The Bessemer process.—The Bessemer "converter," Fig. 36, is a pear-shaped vessel, A, lined with a very refractory siliceous sandstone; it is large enough to hold a charge of 10 tons of molten metal. It is supported on a central axis, and air, led by a pipe, B, from the trunnions, is blown through the charge from twyers with fine openings at the base, C, of the converter. The converter is turned into the horizontal position during the introduction of the molten metal and the blowing commenced; it is then rotated to bring the mouth upwards and the blowing continued. The silicon first undergoes oxidation and then the carbon, the operation lasting about 15 minutes. What remains is practically wrought iron; to convert this into steel, the necessary amount of carbon must be added. This is done by adding a quantity of molten *spiegeleisen*, a substance containing from 5 to 15 per cent. of manganese, and 5 or 6 per cent. of carbon or *ferromanganese*, a similar body which contains 20 per cent. or more of manganese, and then blowing for a short time. The carbon transforms the iron into

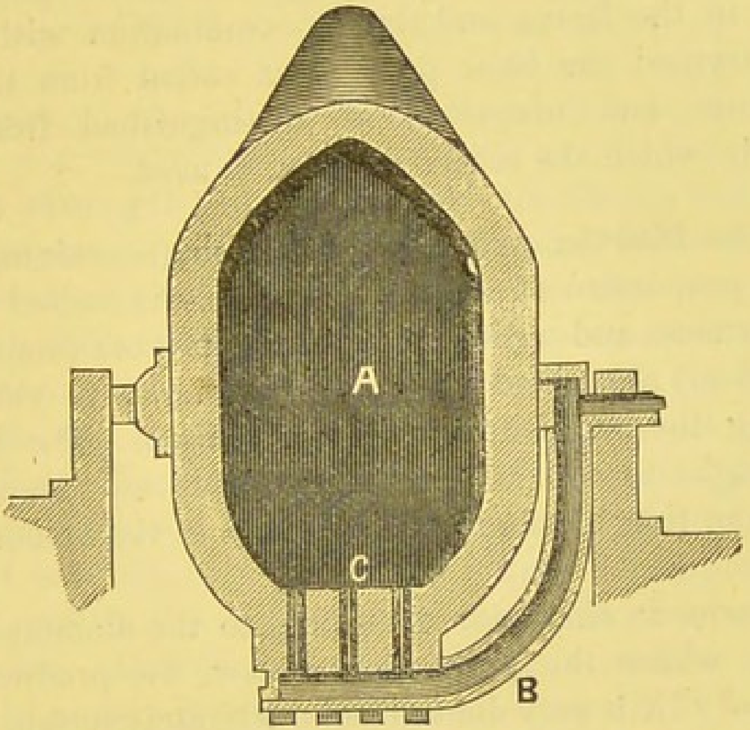


FIG. 36.

steel, the "temper" of which will vary according to the amount so introduced, whilst the manganese increases the malleability. The presence of sulphur in steel has the effect of rendering it brittle when hot ("red-short") and phosphorus makes it brittle when cold ("cold-short"); the addition of manganese counteracts the effect of the sulphur, but if the ore contains more than a minute quantity of phosphorus, a modification of the process must be made in order to eliminate this. Thomas and Gilchrist found that by lining the converter with lime and magnesia instead of silica and adding lime at the last "blow," the phosphorus was retained in the lining and slag in combination with these bases. This is termed the *basic* process, so called from the use of the bases lime and magnesia as distinguished from the *acid* process, in which the siliceous lining is used.

Siemens-Martin process.—Pig iron (containing as it does a larger proportion of carbon than steel) is melted in an open-hearth furnace, and wrought iron and iron ore (containing little or no carbon) are added in such quantities as to yield a product containing the requisite amount of carbon. The heating lasts usually eight to ten hours, and samples are drawn from the charge from time to time and tested as to the amount of carbon present.

Steel varies in character according to the amount of carbon it contains; where the proportion is low, the product is termed "mild steel;" it is very ductile and moderately tough, and capable of being only slightly hardened and "tempered." As the proportion of carbon rises, the ductility shows a falling off but the tenacity increases, though a limit is reached as the carbon approaches 1·5 per cent. when steel resembles cast iron, being hard and brittle.

When a steel of intermediate character is heated to bright redness and suddenly cooled it becomes very hard (glass-hard) and brittle. If in this condition it be again heated to a much lower temperature (between 200° C. and 350° C.) it loses this brittleness and becomes elastic in degrees varying with the particular temperature used. This treatment is called "tempering," and it is employed for bringing the steel into a condition suitable for different classes of tools or appliances according as hardness or elasticity are most to be desired for such appliances.

Composition and properties of wrought iron, cast iron, and steel.—The following table shows the general composition of these products.

	Wrought iron.	Steel.	Cast iron.
Iron	99·5	98·5	92 to 95
Carbon	0·1 to 0·3	0·3 to 1·5	1·5 to 4·5
Sulphur	trace	0·04	0·1
Phosphorus ...	0·2	0·03 to 0·1	0·5
Silicon	nil	0·2	1 to 4
Manganese ...	nil	0 to 1 or more	nil

Tensile strength.—Iron and steel are fibrous and tough, the former possessing a tensile strength of about 25 tons per square inch of section and the latter 30 to 45 tons; cast iron is hard and brittle, its tensile strength being usually between 6 and 10 tons to the square inch. Wrought iron and steel are also highly *malleable* though less so than silver or gold; they are capable of being welded. The *melting point* of all three substances is very high (approximately 1600° to 1800°), that of cast iron being lowest and of wrought iron highest. Iron decomposes steam at a red heat, and in the finely divided condition it even acts upon boiling water. At ordinary temperatures it oxidizes superficially ("rusts") in moist air or in water containing air in solution.

Oxides and hydroxides.—Three oxides of iron are known to exist in the free state, viz. ferrous oxide, FeO, magnetic oxide, Fe_3O_4, and the sesquioxide or ferric oxide Fe_2O_3, whilst a fourth (probably FeO_3) occurs in combination in certain unstable salts, the ferrates of the alkalies and alkaline earths.

Ferrous oxide, FeO, is obtained by reduction of the sesquioxide in hydrogen at 300° C. or by heating the oxalate with the exclusion of air or oxygen. It glows on exposure to air at ordinary temperatures, and readily becomes oxidized to ferric oxide. The *ferrous hydroxide* $Fe(OH)_2$, a white flocculent substance obtained by precipitation of ferrous salts with potash, oxygen being rigidly excluded, also absorbs oxygen with great avidity, turning dark green and ultimately passing into ferric hydroxide, $Fe_2(OH)_6$. Ferrous oxide is a basic oxide, and by the action of the several acids upon it (or upon metallic iron) a series of salts known as the *ferrous salts* are obtained. These salts are usually white in the anhydrous condition and pale green when in the hydrated form.

Ferric oxide (sesquioxide), Fe_2O_3, occurs in considerable deposits either as such or associated with water of hydration. (See p. 209.) It is obtained as a residue when ferrous sulphate is strongly heated, and this residue is employed as a polishing powder or as a pigment under the names colcothar, jeweller's rouge, Venetian red, and yellow, red, or brown ochre, according to its shade. Iron rust consists chiefly of hydrated ferric oxide. The *Hydroxide*, $Fe_2(OH)_6$, is obtained on precipitating ferric salts with alkalies :—

$$Fe_2Cl_6 + 6\ KOH = Fe_2(OH)_6 + 6\ KCl.$$

It forms the base of the *ferric salts.*

Magnetic oxide of iron, Fe_3O_4, occurs as magnetite or lodestone, and is formed when metallic iron is strongly heated in steam or carbon dioxide. It derives its name from the fact of its being magnetic. Strong mineral acids act upon it, forming a mixture of ferrous and ferric salts, and no series of salts corresponding to it has been prepared.

When chlorine is passed into a strong solution of caustic potash in which ferric hydrate is suspended, some of the iron passes into the solution, which becomes purple and contains a compound of a higher oxide of iron, potassium ferrate (K_2FeO_4 ?).

Ferrous sulphide, FeS, is prepared by heating together iron filings and sulphur, or by the reduction of ferrous sulphate by carbon. The precipitated form of it, obtained by adding an alkaline sulphide to a ferrous salt, rapidly undergoes oxidation to ferrous sulphate when exposed to air. Mineral acids act very readily on ferrous sulphide, liberating sulphuretted hydrogen.

Iron pyrites, FeS_2, is found native as iron pyrites and as marcasite ; in contact with moisture and air these become slowly oxidized to ferrous sulphate. When they are heated, sulphur is given off, and in presence of air this undergoes a more or less complete oxidation to sulphur dioxide, ferric oxide being left as a residue.

Ferrous chloride, $FeCl_2$, is obtained in white feathery crystals by heating metallic iron in a current of dry hydrochloric acid. It is deliquescent and readily soluble in water, green crystals having the composition $FeCl_2.4\ H_2O$ separate out when iron is dissolved in hydrochloric acid and the solution is concentrated by evaporation. By treating such a solution with chlorine, the ferrous chloride passes into ferric chloride.

Ferric chloride, Fe_2Cl_6.—This salt is also formed by direct union of iron and chlorine or by dissolving ferric oxide in hydrochloric acid. Ferric chloride can be volatilized without decomposition, its boiling point being about 280° C. ; up to over 400° C. the density of its vapour accords with the composition Fe_2Cl_6, but at higher temperatures it diminishes, and at 750° C. possesses approximately half the above density, corresponding to the composition $FeCl_3$—

VD at 448° = 10·49 VD at 750° = 5·39
Fe_2Cl_6 requires 11·2 (air = 1)
$FeCl_3$,, 5·6 (,,)

Ferric chloride is freely soluble in water, and the solution dissolves freshly precipitated ferric hydrate in such quantity that its composition may reach $Fe_2(OH)_5Cl$; if it be then dialyzed the chlorine is almost entirely removed and the solution of ferric hydrate in the colloidal form is obtained. This is known as "dialyzed iron." A solution of ferric chloride undergoes reduction to ferrous chloride when sulphuretted hydrogen is passed into it.

$$Fe_2Cl_6 + H_2S = FeCl_2 + 2\ HCl + S$$

Metallic iron combines directly with bromine and iodine when triturated with them ; *ferrous bromide*, $FeBr_2$, is thus formed in the manufacture of bromine and a solution of iodine in *ferrous iodide*, FeI_2, is made use of in the production of potassium iodide ;

$$Fe_3I_8 + 4\ H_2O\ 4\ K_2CO_3 = 8\ KI + Fe_3(OH)_8 + 4\ CO_2$$

The simple ferrous and ferric cyanides have not been obtained in a state of purity, but a complex and very important series of double cyanides of iron and K Na, Ba, Cu, etc. has been prepared : the ferrocyanide of potassium ($K_4Fe''Cy_6$) and the ferricyanide of potassium ($K_3Fe'''Cy_6$) are frequently used in testing for the presence of salts of iron. Cyanides of iron of a complex nature may be obtained by the action of these double cyanides on iron salts. Thus if to the ferrocyanide (in excess) ferric chloride be added, or to the ferricyanide (in excess) ferrous chloride be added, a replacement of potassium by iron occurs according to the equations:—

$$K_4Fe''Cy_6 + Fe'''Cl_3 = KFe''Fe'''Cy_6 + 3\,KCl.$$
$$K_3Fe'''Cy_6 + Fe''Cl_2 = KFe''Fe'''Cy_6 + 2\,KCl.$$

The body $KFe''Fe'''Cy_6$ is a dark-blue precipitate identical in the two reactions; it is called *soluble* Prussian blue, as it can be dissolved by water. But if now, soluble Prussian blue be digested with ferric and ferrous chloride respectively (or if these chlorides be originally used in excess) the whole of the potassium is replaced and complex cyanides of iron, viz. *insoluble* Prussian blue and Turnbull's blue, are respectively obtained:—

$$3\,KFe''Fe'''Cy_6 + Fe'''Cl_3 = 3\,KCl + \underset{\text{Insoluble Prussian blue.}}{3\,Fe''Cy_2.4\,Fe'''Cy_3.}$$
$$2\,KFe''Fe'''Cy_6 + Fe''Cl_2 = 2\,KCl + \underset{\text{Turnbull's blue.}}{3\,Fe''Cy_2.2\,Fe'''Cy_3.}$$

The formation of these precipitates, and the fact that ferric salts give no precipitate, but only a brown colouration, when added to ferricyanide of potassium, afford means of detecting the presence of iron and of distinguishing ferrous from ferric salts.

Ferrous sulphate, $FeSO_4 7\,H_2O$, known also as green vitriol, forms green monoclinic crystals, and is obtained by dissolving metallic iron in dilute sulphuric acid (excluding air or oxygen) and then concentrating the solution to the point at which it crystallizes. It is also formed slowly by the oxidation of the mineral marcasite (FeS_2) at ordinary temperatures. When this salt is mixed in solution with alkaline sulphates, and sufficiently concentrated, crystals of a double salt having the composition $M_2SO_4.FeSO_4.6H_2O$ separate out. Ferrous salts in presence of oxidizing agents, such as acidulated solutions of potassium permanganate and potassium bichromate, are converted into ferric salts, and if the amount of the oxidizing agent so used is known, this reaction may be employed for estimating the iron present—

$$10\,FeSO_4 + 2\,KMnO_4 + 9\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + 2\,MnSO_4 + 2\,KHSO_4 + 8\,H_2O$$

$$6\ FeSO_4 + K_2Cr_2O_7 + 8\ H_2SO_4 = 3\ Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 2\ KHSO_4 + 7\ H_2O$$

Comparing the combining weights of the oxidizing agents used with the amount of iron present in the ferrous condition it is seen from the equations that 315·4 parts by weight of potassium permanganate correspond to 560 parts by weight of iron, and 294·8 parts of potassium bichromate correspond to 336 parts of iron. Such interactions between an oxidizable body and an oxidizing agent may be more readily understood by regarding the action as taking place between the respective oxides which really take part in them, thus—

$$10\ FeO + Mn_2O_7 = 5\ Fe_2O_3 + 2\ MnO.$$
$$6\ FeO + 2\ CrO_3 = 3\ Fe_2O_3 + Cr_2O_3.$$

Conversely, a solution of ferrous sulphate or of the double salt ferrous ammonium sulphate, of known strength, may be employed for estimating the amount of an oxidizing agent present. A cold concentrated solution of ferrous sulphate dissolves nitric oxide forming $FeSO_4.NO$, and the dark-brown ring observed in testing for the presence of nitric acid in a solution is due to the presence of this body.

Ferric sulphate, $Fe_2(SO_4)_3$.—When ferrous sulphate is exposed to moist air it is slowly transformed into ferric sulphate, and this change (see previous paragraph) is effected more rapidly in solution in presence of oxidizing agents. Ferric sulphate is formed directly by dissolving ferric oxide (Fe_2O_3) in sulphuric acid. In combination with alkaline sulphates it forms alums isomorphous with ordinary alum ; thus iron ammonium alum has the composition $(NH_4)_2SO_4.Fe_2(SO_4)_3.24\ H_2O$, and differs from ordinary ammonia alum $(NH_4)_2SO_4.Al_2(SO_4)_3.24\ H_2O$ in the replacement of aluminium by iron.

Ferrous and ferric nitrates, $Fe(NO_3)_2$ and $Fe(NO_3)_3$, are prepared by the action of nitric acid on iron, the ferrous salt being obtained when cold dilute nitric acid is employed and the ferric salt when excess of concentrated acid is added. The ferric nitrate obtained in this way, or the product, obtained by the action of nitric acid on ferrous sulphate is used as a mordant in dyeing. Basic salts may be obtained by digesting freshly precipitated ferric hydrate with concentrated aqueous solutions of ferric sulphate or nitrate.

Ferrous carbonate, $FeCO_3$, occurs as already stated as a mineral product. It is formed when an alkaline carbonate is added to a solution of a ferrous salt. In this form it is very unstable and readily parts with carbon dioxide; the ferrous hydroxide thus produced then undergoes oxidation to ferric hydroxide, and the reddish-brown deposit which is found in chalybeate waters is no doubt formed from ferrous carbonate in this way.

Detection and estimation.—Ammonia and the caustic alkalies effect the precipitation of iron from the solutions of its salts as hydroxides, and this when strongly heated in air yields ferric oxide (Fe_2O_3), in which form iron is usually estimated gravimetrically. The volumetric estimation of iron by means of potassium permanganate or bichromate has been already referred to. The presence of iron may also be ascertained by means of ferrocyanide and ferricyanide of potassium. (See p. 218.) Where very small quantities of iron are to be estimated, this may be done by the colourimetric process depending on the depth of tint given by the addition of potassium ferrocyanide (blue) or sulphocyanide (red).

COBALT AND NICKEL.

These elements present so many points of resemblance that it may be advantageous to describe them together.

Occurrence.—The ores are chiefly compounds of the respective metals with arsenic and sulphur:

Speisscobalt, $CoAs_2$ or $(FeCoNi)As_2$, and white nickel ore, $NiAs_2$, corresponding to the arsenide of iron, $FeAs_2$.

Cobalt glance, CoSAs, and nickel glance, NiSAs, corresponding to mispickel, FeSAs.

Kupfernickel, NiAs, millerite, NiS, and garnierite, a double silicate of nickel and magnesium.

Cobalt and nickel bloom, $Co_3.(AsO_4)_2.8\ H_2O$, and $Ni_3(AsO_4)_2$ $8\ H_2O$ corresponding to vivianite, $Fe_3(AsO_4)_2 8\ H_2O$.

Metal.—The arsenical ores are roasted, extracted with hydrochloric acid and treated with sulphuretted hydrogen for the removal of copper, lead, antimony and any remaining arsenic. Bleaching powder is then added in sufficient quantity to fully oxidize the iron so that it is thrown down on the addition of chalk. The solution now contains cobalt and nickel, and a further quantity of bleaching powder effects the precipitation of the cobalt as sesquioxide Co_2O_3, the nickel being ultimately thrown down as oxide by adding milk of lime. From these oxides the metal may be obtained by heating them in a current of hydrogen. Cobalt and nickel are both metals of a grey colour possessing a high degree of malleability and ductility. Nickel is deposited electrolytically from a solution of the nickel ammonium sulphate, $(NH_4)_2SO_4\ NiSO_4.6\ H_2O$, which is used in this way for nickel plating. It also enters as a constituent into many useful alloys, such as German silver and nickel coinage; recently it has been added to steel, increasing its tensile strength and hardness.

Cobalt forms the basis of a number of pigments, such as smalt, Thenard's blue, Rinmann's green, and cobalt yellow. *Smalt* is formed by fusing crude cobaltous oxide ("Zaffre") with quartz and potassium carbonate; *Thenard's blue* and *Rinmann's green* by heating cobalt compounds with alumina and zinc oxide respectively; *cobalt yellow* by the addition of potassium nitrite to an acid solution of nitrate of cobalt.

When nickel is gently heated in a current of carbon monoxide, *nickel carbonyl* $Ni(CO)_4$ is produced. It is a colourless liquid of specific gravity 1·356, which boils at 43° C., the vapour undergoing decomposition at a somewhat higher temperature, yielding a deposit of very pure nickel. Iron forms a similar compound.

Oxides and hydroxides.—Both cobalt and nickel form monoxides and sesquioxides. The *monoxides*, CoO and NiO, are obtained by heating the carbonates, the hydroxides, or the sesquioxides. The corresponding hydroxides are precipitated on the addition of caustic potash to solutions of cobaltous or nickel salts respectively, the cobaltous hydroxide being insoluble in ammonia while the nickel hydroxide is soluble.

The *sesquioxides*, Co_2O_3 and Ni_2O_3, are black powders formed when the precipitation by caustic alkalies takes place in presence of chlorine or hydrogen peroxide. They may therefore be obtained by passing chlorine into a solution of caustic potash in which the monoxides are suspended. These oxides are unstable, and when heated they readily give up oxygen and pass into the lower oxides.

The other compounds of importance are the chlorides, sulphates, and nitrates.

Chlorides.—The anhydrous *chlorides* of cobalt and nickel, $CoCl_2$ and $NiCl_2$, are obtained by the action of chlorine on the metal; they are beautiful feathery crystals, the former of a blue colour and the latter pale buff. They deliquesce in moist air, becoming pink and green respectively. These hydrated forms may be prepared by digesting the metals or the monoxides with hydrochloric acid.

Similarly the *nitrates*, $Co(NO_3)_2$, $Ni(NO_3)_2$, and the *sulphates*, $CoSO_4$, $NiSO_4$, are formed by dissolving the metals or their oxides in nitric and sulphuric acid respectively. The sulphates form double salts with the sulphates of the alkalies resembling the corresponding iron derivatives.

A peculiar property of cobalt is the formation of the *cobalt-amines*. These salts contain ammonia feebly attached and resemble the compounds formed when calcium chloride or silver chloride are exposed to the action of ammonia, and like them they readily dissociate when heated, evolving ammonia.

When ammonia is added to a solution of cobaltous chloride until the precipitate of the hydroxide first formed redissolves, crystals having the composition $CoCl_2.6NH_3.H_2O$ separate out after a time. On oxidation by exposure to air, derivatives of the sesquioxide, Co_2O_3, are obtained—*e. g.* $Co_2Cl_6.10NH_3.5H_2O$, $Co_2OCl_4.8NH_3.3H_2O$, and even of the dioxide CoO_2.—*e. g.* $CoO(NO_3)_2.5\ NH_3.H_2O$.

Detection and estimation.—Both nickel and cobalt are precipitated as sulphides on the addition of ammonium hydrosulphide to neutral or alkaline solutions of their salts. The nickel sulphide is somewhat soluble in the reagent, imparting a brown colour to the liquid. The sulphides are only slowly dissolved by weak hydrochloric acid, and may thus be separated from the readily soluble sulphides of iron, zinc and manganese and the hydroxides of aluminium and chromium. Cobalt compounds impart a bright blue colour to the borax bead in either the oxidizing or reducing flame; they also form the characteristic Thenard's blue and Rinmann's green. (See p. 221.)

The separation of nickel and cobalt may be effected by converting into the double cyanides, cobalt forming the stable potassium cobalticyanide K_3CoCy_6, whilst nickel forms K_2NiCy_4; on now warming, with caustic soda in presence of chlorine (sodium hypochlorite), the nickel compound is decomposed and nickel is precipitated as the black hydroxide of the sesquioxide Ni_2O_3, whilst the cobalt remains in solution, since the potassium cobalticyanide does not suffer decomposition. Cobalt may also be separated from nickel by precipitation with potassium nitrite. (See p. 221.)

CHAPTER XIV.

MANGANESE.

Though the compounds of chromium, iron, ruthenium, and osmium show in some respects analogies to those of manganese, there are yet no sufficient grounds for including manganese in the groups to which these metals belong. Chlorine, according to Mendelejeff's classification, stands related to manganese in the same way that sulphur does to chromium, and the resemblance is further borne out by the fact that the perchlorates are isomorphous with the permanganates just as the sulphates are isomorphous with the chromates (and manganates). In its lower oxides and the derivatives corresponding to them, manganese shows more analogy to iron.

Occurrence.—The chief minerals containing manganese are the *oxides*, pyrolusite, MnO_2, braunite, Mn_2O_3, and hausmannite Mn_3O_4; the *carbonate*, $MnCO_3$ is often found associated with ferrous carbonate in spathic iron ores.

Metal.—The oxides of manganese are more difficult to reduce than those of iron; to obtain the metal it is necessary to mix the oxide intimately with carbon and expose to a very high temperature. The metal is very readily oxidized and slowly decomposes water at ordinary temperatures, the decomposition proceeding rapidly in boiling water. It is not largely used, its chief application being in the production of ferromanganese; it enters also as an essential constituent of spiegeleisen. (See p. 213.)

Manganous oxide, MnO, is obtained by igniting the carbonate or any of the higher oxides in a current of hydrogen; the corresponding hydroxide, $Mn(OH)_2$ is precipitated when caustic alkalies are added to a solution of a manganous salt.

$$MnCl_2 + 2\ KOH = Mn(OH)_2 + 2\ KCl.$$

It is almost white, but in contact with air it rapidly oxidizes and turns brown. Manganous oxide is a basic oxide and dissolves in mineral acids forming salts such as manganous chloride, $MnCl_2$, sulphate, $MnSO_4$, and nitrate, $Mn(NO_3)_2$.

Trimanganese tetroxide, Mn_3O_4, is obtained when any oxide of manganese is strongly heated in presence of air, and is therefore the form in which manganese is gravimetrically estimated. Heated with sulphuric acid it dissolves, forming manganous sulphate and giving off oxygen, whilst, with hydrochloric acid, chlorine is evolved—

$$Mn_3O_4 + 8\ HCl = 3\ MnCl_2 + Cl_2 + 4\ H_2O.$$

Manganese sesquioxide, Mn_2O_3, is obtained as a passage product on heating manganous nitrate, the ultimate product being Mn_3O_4. Like the corresponding oxides of iron and aluminium it forms an alum with the sulphate of the alkalies—*e. g.* $K_2SO_4.Mn_2(SO_4)_3.24H_2O$. With hydrochloric acid it reacts according to the equation—

$$Mn_2O_3 + 6\ HCl = 2\ MnCl_2 + Cl_2 + 3\ H_2O.$$

Manganese dioxide, MnO_2.—The hydroxide may be prepared by the addition of caustic alkalies to manganese salts in presence of chlorine (or a hypochlorite), or by agitating manganous hydroxide with chlorine water—

$$2\ Mn(OH)_2 + Cl_2 = MnCl_2 + Mn(OH)_4.$$

When warmed with hydrochloric acid, manganous chloride is formed and chlorine given off—

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

Comparing the action of the last three oxides on hydrochloric acid, it is seen that whilst with Mn_3O_4 only $\frac{1}{4}$ of the chlorine of the hydrochloric acid is evolved as chlorine, and with Mn_2O_3 only $\frac{1}{3}$, the oxide MnO_2 gives a yield of $\frac{1}{2}$ the chlorine. Manganese dioxide is thus the best material for giving a high yield of chlorine, and it is largely used for this purpose in the manufacture of bleaching powder.

Manganese dioxide may be used as a source of oxygen, either by heating it by itself or mixed with sulphuric acid.

With strong bases MnO_2 forms *manganites*, of which $CaMnO_3$ may be taken as an example. The residual liquors from the chlorine production on the large scale contain manganous chloride, and the manganese may be recovered from such liquors by the Weldon recovery process. This consists essentially in the precipitation of the manganous hydroxide by excess of lime, and the oxidation of this in presence of lime by blowing air through it; most of the manganese is transformed into calcium manganite, which is then available for the further production of chlorine by acting upon it with hydrochloric acid.

$$CaMnO_3 + 6HCl = CaCl_2 + MnCl_2 + Cl_2 + 3\ H_2O.$$

Manganese trioxide, MnO_3.—Compounds which contain the group MnO_3 in combination, such as potassium manganates, K_2MnO_4, and the oxyhaloids MnO_3F, MnO_3Cl, have long been known, but it is only quite recently that evidence has been obtained of the oxide in the free state. Wöhler had noticed that when concentrated sulphuric acid is poured on solid potassium permanganate, violet vapours were given off, which he thought must be due to permanganic acid. Franke has shown that if the green solution obtained by dissolving potassium permanganate (probably $(MnO_3)_2SO_4$) be dropped upon dry sodium carbonate, violet vapours are given off, the composition of which seems to agree with the formula MnO_3. They readily undergo decomposition, especially in presence of moisture.

Manganic acid, H_2MnO_4, of which this oxide may be regarded as the anhydride, is not known in the free state. The manganates of the alkalies may, however, be prepared by fusing manganese dioxide with excess of a caustic alkali, or any manganese compound with alkalies in presence of an oxidizing agent such as potassium nitrate. They are of a dark green colour, and dissolve in water to form green solutions. In presence of free alkali they are stable, but the weakest acids, even CO_2, transform them into permanganates.

Manganese heptoxide, Mn_2O_7, is a brown liquid which separates on adding potassium permanganate in proper proportions to concentrated sulphuric acid. It may be looked upon as the anhydride of permanganic acid, $H_2Mn_2O_8$. It is a powerful oxidizing agent, and like perchloric acid decomposes in contact with dry organic matter, the carbon being oxidized so rapidly that it usually takes fire.

The *permanganates* of the alkalies are obtained by acidulating solutions of the manganates. They are readily soluble in water, yielding deep purple solutions. In acid solution, $2KMnO_4$ give up 5 atoms of oxygen in presence of reducing agents (see p. 218), and this salt is used in estimations by volumetric methods.

As further instances of its behaviour may be given :—

(1) Its action on potassium iodide :

$$2\,KMnO_4 + 10\,KI + 14\,H_2SO_4 = 12\,KHSO_4 + 2\,MnSO_4 + 10\,I + 8\,H_2O$$

(2) Its action on peroxides :

$$2\,KMnO_4 + 5\,Na_2O_2 + 14\,H_2SO_4 = 2\,KHSO_4 + 10\,NaHSO_4 + 2\,MnSO_4 + 5\,O_2 + 8\,H_2O$$

this reaction being quite comparable to that which occurs in presence of free hydrogen peroxide (see p. 73).

(3) Its action on oxalic acid or oxalates :

$$2\,KMnO_4 + 5\left\{\begin{matrix}COOH\\COOH\end{matrix}\right. + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O$$

$$2\,KMnO_4 + 5\left\{\begin{matrix}COOK\\COOK\end{matrix}\right. + 14\,H_2SO_4 = 12\,KHSO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

(4) Its action on concentrated solutions of hydrochloric acid :

$$2\,KMnO_4 + 16\,HCl = 2\,KCl + 2\,MnCl_2 + 5\,Cl_2 + 8\,H_2O.$$

All these reactions may, like that with ferrous salts already referred to, be more readily understood by considering them as taking place between the substances in question and the oxide Mn_2O_7.

Manganous sulphide, MnS, in the anhydrous condition, is a green amorphous substance, but in the hydrated form, as precipitated from solutions of manganese salts by an alkaline sulphide, it is flesh coloured.

Nitride of manganese, Mn_5N_2, is formed when finely divided manganese is heated in nitrogen ; if ammonia be substituted for nitrogen, a second nitride, Mn_3N_2, is obtained. Manganese, like iron, also combines directly with carbon to form a *carbide.*

Manganous chloride, $MnCl_2$, is the only chloride that has been isolated ; however, an ethereal solution of hydrochloric acid to which manganese dioxide has been added, if kept sufficiently cool, reacts as though it contained a higher chloride, probably Mn_2Cl_6. Manganous chloride is the final product in all cases where the oxides or carbonate are treated with hydrochloric acid. It is a pink salt, and forms double salts with the alkaline chlorides.

Manganous sulphate, $MnSO_4$, is prepared by dissolving manganous oxide or carbonate in sulphuric acid, and likewise forms double salts with sulphates of the alkalies.

Detection and estimation.—Manganese gives in the oxidizing flame an amethyst colour to the borax bead; in the reducing flame the bead gradually becomes colourless. The formation of the sky blue (in traces) or green manganate (see p. 226) is a very delicate reaction for the presence of manganese, as also is the formation of a purple solution of permanganate on boiling manganese compounds (free from chlorine) with nitric acid and lead peroxide. Manganese may be estimated as manganous oxide or sulphide, but it is more usual to make use of the interaction of the dioxide with hydrochloric acid (determining the chlorine given off) or that of permanganate with reducing agents of definite composition, such as $FeSO_4$, or oxalic acid.

CHAPTER XV.

CHROMIUM.

Occurrence.—The chief minerals containing chromium are chrome ironstone, $FeO.Cr_2O_3$, and lead chromate, $PbCrO_4$.

Metal.—This is obtained (*a*) by strongly heating an intimate mixture of the sesquioxide (Cr_2O_3) and charcoal, using especial care to exclude air ; (*b*) by heating the corresponding chloride, Cr_2Cl_6, with metallic zinc under a layer of common salt and then dissolving out the excess of zinc by means of nitric acid (HCl dissolves chromium); (*c*) by similar treatment of a mixture of potassium chloride and the double chloride of potassium and chromium ($2\ KCl.Cr_2Cl_6$) with metallic magnesium.

The metal is very hard, difficult to fuse, and is not magnetic; it burns with great brilliancy when strongly heated in air or oxygen. When alloyed with iron or steel it confers greater hardness, elasticity, and tenacity.

Oxides and hydroxides.—The lowest oxide *chromous oxide*, CrO, has only been obtained in the hydrated form by adding caustic potash to the chromous chloride, $CrCl_2$. It possesses basic characters, and chromous acetate is formed by the action of sodium acetate on chromous chloride ; it takes up oxygen eagerly and may be used for freeing gases from traces of oxygen. Chromous sulphate, $CrSO_4$, is obtained by dissolving metallic chromium in sulphuric acid.

Chromium Sesquioxide, Cr_2O_3, may be prepared as a dark green powder by heating ammonium bichromate $(NH_4)_2Cr_2O_7$ or a mixture of potassium bichromate and ammonium chloride and washing out the potassium chloride which is formed. The hydroxide $Cr_2(OH)_6$ is precipitated when the green or violet solution of chromium salts (*i. e.* the sesqui-salts) are boiled with caustic alkalies. Several important green pigments, such as emerald green and Guignet's green, consist essentially of the sesquioxide. It is also employed in porcelain painting and in colouring glass. The hydroxide dissolves freely in the sesquichloride, Cr_2Cl_6, just as ferric hydroxide does in ferric chloride, and on dialyzing such a solution, it, like iron, yields a hydroxide solution in water.

By dissolving the hydroxide in sulphuric acid, a green or violet solution is obtained containing the *sesquisulphate* $Cr_2(SO_4)_3$, and this when mixed with potassium or ammonium sulphate yields double salts of a deep purple colour analogous to the alums and isomorphous with them. The properties of these bodies may be studied by using the potassium chrome alum, $K_2SO_4Cr_2(SO_4)_3$ $24H_2O$. When dissolved in the cold, the solution has a violet colour, which however goes green slowly at ordinary temperatures and quickly when it is boiled. Similarly the chloride and sulphate also form green and violet solutions. Towards reagents the green solutions react differently to the violet, the chlorine or the sulphuric acid they contain is only partially precipitated on the addition of silver nitrate and barium chloride respectively; also sodium phosphate produces no precipitate at first in the green solutions, but in the violet solutions the precipitation occurs immediately. Furthermore it is only the violet solution of the chromium sesquisulphate from which alums can be formed, the green solution yields a double salt of the composition $K_2SO_4.Cr_2(SO_4)_3$ in which barium chloride yields no immediate precipitate. The remarkable fact that there exist salts from which sulphuric and hydrochloric acid fail to be precipitated by the usual reagents has puzzled chemists for a long time; the peculiarity has been ascribed to the existence in combination of isomeric forms of chromium sesquioxide or to a difference of character according to the amount of water of hydration present. A more probable explanation is that this oxide of chromium, like the oxides of molybdenum and tungsten, forms complex acids with the mineral acids, and that $K_2SO_4.Cr_2(SO_4)_3$ for instance contains a very stable chromosulphuric acid $H_2Cr_2(SO_4)_4$, of which the above is the potassium salt.

Chromium trioxide, CrO_3, is formed by the action of sulphuric acid in excess on a strong solution of a chromate or bichromate ; the alkaline chromates in aqueous solution however first pass into bichromates—

$$(1)\ PbCrO_4 + H_2SO_4 = PbSO_4 + CrO_3 + H_2O.$$

$$(2)\left\{\begin{array}{l} \underset{\text{Potassium chromate}}{2\ K_2O.CrO_3} + 2\ H_2SO_4 = \underset{\text{Potassium bichromate.}}{K_2O(CrO_3)_2} + 2\ KHSO_4 + H_2O \\ K_2O(CrO_3)_2 + 2\ H_2SO_4 = 2\ CrO_3 + 2\ KHSO_4 + H_2O. \end{array}\right.$$

The trioxide separates out in beautiful scarlet crystals, which must be freed as completely as possible from the mother liquor at the pump and finally washed with concentrated nitric acid. The oxide decomposes into Cr_2O_3 and oxygen at 250° C., and is a powerful oxidizing agent owing to the readiness with which it parts with oxygen; alcohol dropped upon it takes fire immediately, and it effects the decomposition of ammonia and of organic substances. Ullgren's method of estimating the carbon present in steel is based on the fact that chromium trioxide (or a mixture of potassium bichromate and sulphuric acid) transforms the carbon into carbon dioxide, the amount of carbon dioxide being easily determined by absorption in caustic potash. By saturating an aqueous solution of chromic acid with ammonia and then allowing the product to evaporate, crystals of ammonium chromate $(NH_4)_2CrO_4$ are obtained.

Potassium chromate, K_2CrO_4, may be prepared by fusing chrome iron-stone or chromium sesquioxide with potassium carbonate and nitrate or by passing chlorine into a hot solution of potash in which the precipitated chromium hydroxide is suspended. Insoluble chromates are formed by precipitation—

$$K_2CrO_4 + BaCl_2 = 2\ KCl + BaCrO_4.$$

Potassium bichromate, $K_2Cr_2O_7$.—When sulphuric acid is added to a solution of potassium chromate, the yellow solution darkens, and on concentration crystals of the bichromate (much less soluble than the chromate) separate out. When the bichromate is treated with CrO_3, the *trichromate* $K_2Cr_3O_{10}$ is formed, and if it be dissolved in hot concentrated nitric acid the *tetrachromate* $K_2Cr_4O_{13}$ is obtained.

Perchromic acid, $HCrO_4$ (?) occurs in the bright blue ethereal solution obtained by shaking up with ether an acidulated solution of potassium chromate to which hydrogen peroxide has been added.

Nitride and phosphide of chromium, Cr_2N_2 and **Cr_2P_2**, are obtained by the direct union of chromium with nitrogen and phosphorus respectively. *Carbides* of the composition Cr_4C and Cr_3C_2 are likewise formed by strongly heating chromium in presence of carbon. They are extremely hard and are not attacked even by aqua regia.

Chromous chloride, $CrCl_2$, is produced by heating chromium to redness in hydrochloric acid gas. If to a solution of potassium bichromate excess of zinc be added and concentrated hydrochloric acid be then run in, a beautiful sky-blue liquid is obtained, owing to the formation of chromous chloride. Oxygen acts upon it immediately and the preparation must be made in a vessel from which the air has been displaced by carbon dioxide, the hydrochloric acid being supplied from a stoppered funnel. This reagent is used for the removal of oxygen from admixture with other gases.

Chromium sesquichloride, Cr_2Cl_6, is a very stable body, which can be sublimed without decomposition, and its vapour at 1300° C. has a density corresponding to the formula $CrCl_3$. It is reduced to chromous chloride when heated in hydrogen, but it resists the action of strong mineral acids. It is obtained in bright purple scales by heating a mixture of the sesquioxide and carbon in a current of chlorine. When chromic hydroxide is evaporated down with hydrochloric acid, a green hydrated chloride, $Cr_2Cl_6.2\,H_2O$, is obtained, which when sublimed yields a purple chloride identical with the above.

The chloride, $CrCl_6$, corresponding to the trioxide has not been prepared, but the *oxychloride*, CrO_2Cl_2, is well known as a reddish brown liquid which distils over when a dry mixture of a soluble chloride and potassium bichromate is heated with concentrated sulphuric acid. It is best prepared by dissolving the trioxide in concentrated sulphuric acid, and adding hydrochloric acid drop by drop, and gently warming the mixture.

$$CrO_3 + 2\ HCl = CrO_2Cl_2 + H_2O.$$

The water formed in the reaction is retained by the sulphuric acid. Chromyl chloride is a powerful oxidizing and chlorinating agent; in presence of moisture it decomposes according to the equation—

$$CrO_2Cl_2 + 2\ H_2O = 2\ HCl + H_2CrO_4.$$

Chromium forms compounds with the remaining halogens, very much resembling those which it forms with chlorine. In the case of fluorine, a *hexafluoride*, CrF_6, is prepared by acting on a mixture of lead chromate and calcium fluoride with concentrated sulphuric acid. It reacts with water in a singular manner, giving rise to two acids—

$$CrF_6 + 4\ H_2O = 6\ HF + H_2CrO_4.$$

Detection and estimation.—Chromium compounds colour the borax bead green in both oxidizing and reducing flames. From the chromous or sesqui-salts, the corresponding hydroxide is precipitated by caustic alkalies. Substances containing chromium yield a yellow mass (chromate) when fused with alkaline carbonates and nitre. The salts of the trioxide, CrO_3, are not precipitated by alkalies, but on boiling with excess of concentrated hydrochloric acid, or with alcohol, or by the action of reducing agents, such as H_2S or SO_2, they are transformed into the lower forms of oxidation (sesqui-salts), becoming green, and the chromium is then precipitated by alkalies.

Silver nitrate precipitates the bright red silver chromate from neutral solutions of the chromates and lead nitrate precipitates the yellow lead chromate.

Chromium is estimated as Cr_2O_3, obtained by igniting the precipitated hydroxide.

CHAPTER XVI.

TIN GROUP.

Sn, Pb.

General Characters.—

1. The *metals* are white, easily fusible and not readily affected by exposure to air at ordinary temperatures.

2. The *oxides* of the forms RO and RO_2 are known ; the first are of a basic character, and hence the tendency to the formation of oxy-salts is shown ; the second are predominantly acidic, with hydroxides of variable solubility in the sub-group.

3. The elements combine directly with chlorine to form *dichlorides* and *tetrachlorides.* The *tetrafluorides* form with the alkaline fluorides a well-defined series of isomorphous double salts, $2MF.RF_4$. The members of the group form tetraethides and tetramethides, $R(C_2H_5)_4$ and $R(CH_3)_4$.

TIN.

Occurrence.—Though occasionally found in the metallic condition (Siberia and Guiana) the chief ore is tinstone, SnO_2, which is found in large quantity in Devon and Cornwall, in the Straits Settlements, Saxony and other localities.

Metal.—To obtain this, the tinstone is crushed and the lighter gangue washed away ; it is then roasted to remove any arsenic or sulphur. The reduction takes place easily and is effected by heating the ore in a reverberatory furnace with about one-fifth its weight of anthracite and a little lime or fluorspar. The final purification consists in melting the metal and running it off in the molten condition (the process of liquation) from a dross containing much iron and arsenic, and finally stirring the molten metal with green wood, by which any remaining slag is carried to the surface and the reduction is rendered complete.

It is a white malleable metal melting at about 230° C. Concentrated hydrochloric acid dissolves it readily, forming *stannous chloride,* $SnCl_2$ but concentrated nitric acid is almost without action upon it; dilute nitric acid however dissolves it, and the hydroxide, known as *metastannic acid*, $H_2O(SnO_2)_5.4\,H_2O$, separates out on boiling. When calcined in air, the *dioxide* SnO_2 is obtained as a white insoluble powder.

Alloys.—Tin is largely used for plating iron and also as a constituent of many important alloys. With copper it forms gun-metal, speculum-metal, bell-metal, and bronze ; with lead it forms solder and pewter. Britannia-metal is an alloy of tin, antimony and copper, and with mercury, tin yields an amalgam which is used for producing the bright reflecting surface on glass mirrors.

Oxides and hydroxides. The *stannous hydroxide* is a white powder precipitated on the addition of sodium carbonate to stannous chloride; it readily takes up oxygen on exposure to the air, but if gently heated in carbon dioxide, a black powder, *stannous oxide*, SnO, is obtained.

Stannic oxide, SnO_2, is a white powder which may be prepared by heating metallic tin in the air or by the action of nitric acid on tin. It is insoluble in water and acids and is used for polishing glass.

There are two stannic hydroxides, and as these have acid properties, readily combining with alkalies to form salts, they have been termed acids, viz. *stannic acid* and *metastannic acid.*

Stannic acid, H_2SnO_3, is obtained by the action of caustic soda on stannic chloride, $SnCl_4$, or by the decomposition of sodium stannate Na_2SnO_3 with hydrochloric acid. Sodium stannate may be prepared by fusing stannic oxide with caustic soda ; it is used in dyeing operations as a mordant.

Metastannic acid, $5(H_2SnO_3)$? is very probably a polymer of stannic acid. It is formed, as already mentioned, when tin is dissolved in nitric acid, also by boiling stannic acid with dilute hydrochloric acid, whilst, on the other hand, metastannic acid is converted into stannic acid by the action of alkalies. The stannates crystallize much more readily than the metastannates.

Sulphides.—The compounds of sulphur with tin have a similar composition to those of oxygen. *Stannous sulphide*, SnS, is obtained as a dark brown powder when sulphuretted hydrogen is passed into a solution of a stannous salt or by direct combination of tin and sulphur. *Stannic sulphide*, SnS_2, is formed as a light yellow powder when sulphuretted hydrogen is passed into a solution of a stannic salt. Unlike stannous sulphide, it dissolves readily in alkaline hydrosulphides forming *thiostannates*, R_2SnS_3, and these on treatment with mineral acids undergo decomposition with the precipitation of stannic sulphide. Prepared in the dry way by heating a mixture of finely divided tin with sulphur and ammonium chloride, stannic sulphide is obtained in golden spangles, known as "mosaic gold."

Stannous chloride, $SnCl_2$, is obtained by heating tin in gaseous hydrochloric acid or by driving off the water from "tin salts," $SnCl_2.2H_2O$, a preparation largely used as a reducing agent for indigo, and made by dissolving tin in hydrochloric acid.

Stannic chloride, $SnCl_4$, is a heavy colourless liquid which fumes strongly in air, formed by heating tin in chlorine or with excess of mercuric chloride. In conjunction with small quantities of water it forms crystalline hydrates, and when added to a solution of ammonium chloride, colourless octahedra separate out, of the composition Am_2SnCl_6 analogous to Am_2PtCl_6. *Bromides* and *iodides* of tin corresponding to the chlorides have also been prepared; the *tetrafluoride*, SnF_4, forms a well-defined double salt with potassium fluoride, having the composition $2KF.SnF_4$ isomorphous with the double fluorides of the other elements in this group.

Detection and estimation.—The compounds of tin yield beads of the metal when heated on charcoal in the reducing flame; the metal may be recognized by its malleability and by leaving the insoluble oxide when treated with nitric acid. If a trace of a copper salt be introduced into a borax bead so as to give it the faintest blue tinge and this be heated in presence of tin or its salts it will assume a ruby red colour. Tin is usually estimated as stannic oxide, obtained by boiling to dryness with nitric acid.

LEAD.

Occurrence.—The chief ore from which lead is extracted is galena, PbS. It is very widely distributed and is worked in various parts of the United Kingdom, especially in the northern and south-western counties of England, in Flintshire, and in the Leadhills, Scotland. On the Continent, lead is extracted in the Harz, in Carinthia, Spain, Belgium and other localities; in parts of America, Australia, and Africa there are also considerable deposits of lead ores. The less common ores are cerussite, $PbCO_3$, pyromorphite, $3Pb_3(PO_4)_2.PbCl_2$, and anglesite, $PbSO_4$.

Metal.—In treating of the metallurgy of lead we shall deal with the methods employed in its extraction from galena as the chief source of the metal. For the *richer ores* the first part of the process is carried on in a reverberatory furnace at a moderate temperature whereby *part* of the galena is converted into oxide and sulphate—

$$(1)\quad 2\,PbS + 3\,O_2 = 2\,PbO + SO_2$$
$$(2)\quad PbS + 2\,O_2 = PbSO_4$$

The temperature is then raised and the remaining sulphide reacts by double decomposition with the oxide and sulphate formed in the first stage—

$$(3)\quad PbS + 2\,PbO = 3\,Pb + SO_2$$
$$(4)\quad PbS + PbSO_4 = 2\,Pb + 2\,SO_2$$

With the exception of about 10 per cent. which remains in the "slags" the lead is thus obtained in the metallic condition. After running off the lead, the residue in the slags is extracted by adding lime and a little coal and submitting the mixture to further heating.

The *poorer ores* are usually treated in a small blast furnace or cupola, and this method may be employed for the working of slags. In this case iron or ferrous silicate is the active agent in the removal of sulphur, and the lead obtained contains considerable quantities of silver, copper, antimony, and other metals. Such a process is in use in Germany at Clausthal and Freiberg.

For the working of richer ores a reverberatory furnace of the type known as the Flintshire furnace, Fig. 37, is employed. The essential elements in the construction of such a furnace are, as shown in the figure—

(A) the hopper at which the charge is introduced.

(B) the fire-place at one end and separated from the hearth by a rather high fire-bridge.

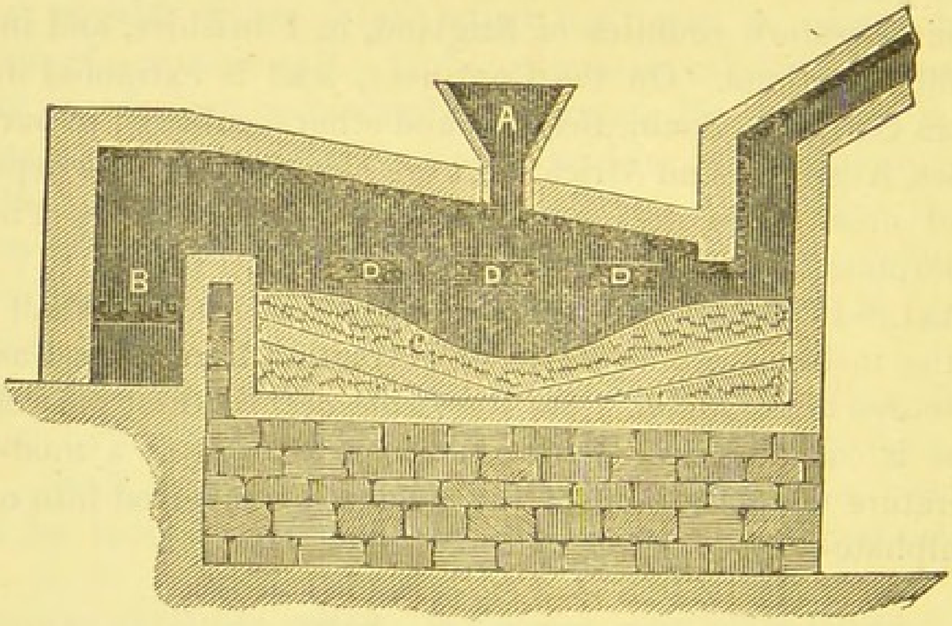


FIG. 37

(C) the hearth formed by moulding slag into the form shown, the depression serving for the collection of the molten lead and the slopes of the hearth for spreading the charge so as to expose it to the action of the fire gases and for working the slags.

(D) the doors for regulating the supply of air and working the charge.

The first part of the process is carried out at dull red heat, and is essentially one of calcination and oxidation during which reactions (1) and (2) take place. The doors are then closed and the temperature raised to a full red heat, when reactions (3) and (4) are effected.

Another form of furnace, known as the "Scotch hearth," largely used in the north of England, differs essentially from the above in that the hearth is shallow and that a blast is provided. The success of the process depends on the proper admixture of the fresh ore with that which has undergone oxidation and in the regulation of the supply of air and fuel. The changes consist partly in those described above, viz. the oxidation of part of the ore and the double decomposition which takes place between this and the fresh ore, and partly in reduction by the fuel added. Figure 38 shows in section the form of hearth in use in Scotland and the north of England, the essential parts being—

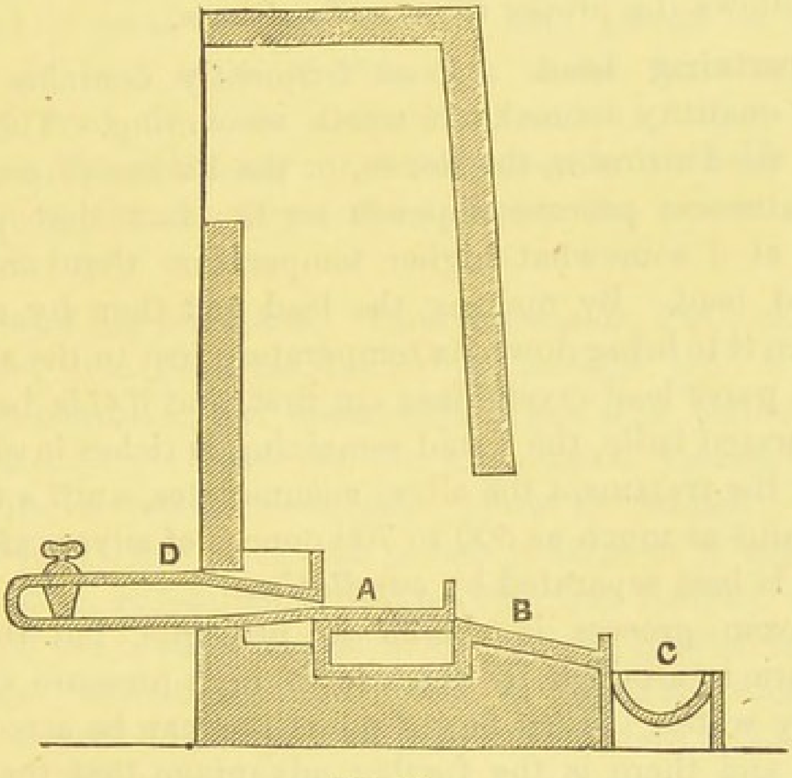


FIG. 38.

(A) the hearth, about 4 to 6 inches deep.

(B) the work-stone provided with a shallow rim and a diagonal groove for running off the lead.

(C) the pot for the reception of the metal.

(D) the twyer, at the back of the hearth, for providing the blast.

Slags are usually worked up separately in a furnace of a similar type but having a shaft above the hearth some three feet high in which the slags and fuel are placed as in a blast furnace.

The lead obtained by any of these processes frequently contains sufficient antimony (as well as tin, copper, iron, silver, etc.) to render it hard, and it is in this case submitted to a process of *softening*. The metal is heated on the bed of a reverberatory furnace until the antimony (copper, etc.) becomes oxidized and forms a scum on the surface. This is skimmed off along with litharge which collects with it and the process continued until the lead shows the proper degree of softness.

Desilverizing lead. Lead frequently contains silver in sufficient quantity to make it worth recovering. This is done by either the Pattinson, the Rozan, or the Parkes process.

The Pattinson process depends on the fact that pure lead solidifies at a somewhat higher temperature than an alloy of silver and lead. By melting the lead and then by sprinkling water upon it to bring down its temperature just to the solidifying point, the purer lead crystallizes out first, and if this be removed by a perforated ladle, the liquid remaining is richer in silver. By repeating the treatment the silver accumulates, until a ton of the lead contains as much as 600 to 700 ounces of silver, after which the silver is best separated by *cupellation*.

The Rozan process is similar in principle, but the proper temperature is attained by the use of high-pressure steam and cooling by water. Much larger quantities can be acted upon at one time, and there is the further advantage that the extreme agitation and contact with air promote the removal of antimony and other impurities at the same time.

In the Parkes process, zinc is added to the metal in suitable proportions, an alloy of lead, zinc, and silver in this case solidifying whilst the lead free from silver remains molten.

Cupellation.—For obtaining the silver free from lead, the metal is heated in an oxidizing atmosphere on a *cupel*, *i. e.* in a special furnace, the bed of which is made of bone-ash impregnated with pearl-ash. The lead is oxidized to litharge, which collects at the surface of the charge and is blown off or to some extent absorbed by the bed of the furnace, carrying with it the impurities and leaving molten silver.

Properties of the metal.—Lead is a soft bluish-grey metal with a bright lustre at a freshly cut surface. It tarnishes in air and is also superficially acted upon by water, especially in presence of carbon dioxide or in water containing certain salts in solution. It is very malleable but possesses very little tenacity.

Alloys.—Lead is an essential constituent of several common alloys. *Solder* is an alloy of lead and tin, the proportions of the metals used varying between the limits, 2 parts of tin to 1 part of lead and 2 parts of lead to 1 of tin; *pewter* is an alloy of 1 part of lead to 4 of tin; *type metal* is composed of 4 parts of lead to 1 of antimony; and an alloy of these metals with the antimony predominating is used in the construction of appliances where resistance to the action of strong acids is called for.

Oxides and hydroxides. *Lead monoxide*, PbO, called also massicot and litharge, is obtained when metallic lead is oxidized at high temperatures, the massicot being a dull yellow powder and the litharge (obtained in the cupellation process) a flaky mass, varying in colour from pale yellow to reddish. When a solution of lead oxide in caustic potash is allowed to cool slowly, a yellow oxide, crystallizing in the rhombic system, separates out, whilst if the cooling be still more gradual, reddish tetragonal crystals are formed; lead monoxide is therefore dimorphous. The oxide is used in the production of flint glass and as a glaze for pottery. When ammonia is added to solutions of the salts of lead, the *hydroxide*, $Pb(OH)_2$, is precipitated. This hydroxide is somewhat soluble in water with an alkaline reaction, and, like the caustic alkalies, it absorbs carbon dioxide.

Red Lead or **Minium, Pb_3O_4**, is prepared by the oxidation of massicot, a moderate temperature and free contact with air being essential to its production. When red lead is strongly heated, it becomes darker in colour, and ultimately gives up a part of its oxygen forming the monoxide. When treated with dilute nitric acid, a brown powder, the *lead dioxide*, PbO_2, is left as a residue. This has led to the view that red lead should be regarded as a compound of the monoxide and the dioxide $(PbO)_2PbO_2$. The action of nitric acid is then—

$$(PbO)_2PbO_2 + 4\ HNO_3 = 2\ Pb(NO_3)_2 + PbO_2 + 2\ H_2O.$$

Similarly the *sesquioxide*, Pb_2O_3, may be regarded as $PbO.PbO_2$, and this likewise yields the dioxide on treatment with dilute nitric acid.

Lead dioxide or **peroxide, PbO_2**, is a brown powder obtained as already described, or by the action of chlorine on the oxide suspended in water, or on a solution of a lead salt in presence of free alkali—

$$PbO + NaOCl = NaCl + PbO_2.$$

When strongly heated it gives off oxygen, and passes ultimately into the monoxide. It combines directly with sulphur dioxide, forming lead sulphate with such energy that the product becomes red hot. If lead dioxide be fused with caustic potash, direct combination takes place with the formation of potassium plumbate, K_2PbO_3.

Lead sulphide, PbS, is obtained by direct union of the elements, or by the action of sulphuretted hydrogen on solutions of lead salts. By the action of nitric acid, or even by exposure of the moist sulphide to air at the ordinary temperature, it becomes oxidized to *lead sulphate*, $PbSO_4$.

Lead chloride, $PbCl_2$, is the white precipitate formed when hydrochloric acid or a soluble chloride is added to a solution of a salt of lead. It is slightly soluble in cold water, but much more freely in hot water, from which on cooling the chloride separates in glittering plates. Several basic chlorides are formed either by the addition of ammonia or lime water to solutions of lead chloride, or by fusing oxide of lead with the chloride. One of these, $Pb(OH)Cl$, known as Pattinson's white, is used as a pigment, and is obtained by boiling milk of lime with chloride of lead.

The **tetrachloride, $PbCl_4$**, is a very unstable body obtained by the action of chlorine on the dichloride suspended in hydrochloric acid. With ammonium chloride it forms a double salt of the composition $2AmCl.PbCl_4$.

The **bromide, $PbBr_2$**, and **iodide, PbI_2**, are, like the chloride, obtained by acting on the salts of lead with the respective acids or their soluble salts. They also resemble the chloride in being much more soluble in hot water than cold, and in forming basic salts.

Lead sulphate, $PbSO_4$, is one of the most insoluble of the lead salts; it dissolves readily in caustic alkalies, and slightly in moderately concentrated sulphuric acid, separating out again when the acid is largely diluted.

Lead nitrate, $Pb(NO_3)_2$, is obtained in white crystals by dissolving the metal or its oxide or carbonate in dilute nitric acid, and concentrating the solution until on cooling it crystallizes.

Lead carbonate, $PbCO_3$, or basic carbonates of variable composition, are precipitated when sodium carbonate is added to a solution of lead nitrate. The basic carbonate known as "white lead" is of great importance in consequence of its application as a white pigment. If a solution of lead acetate (sugar of lead) be boiled with lead oxide and then filtered, a basic acetate is obtained, and on passing carbon dioxide through the solution a white precipitate of this basic carbonate, essentially $(PbCO_3)_2 Pb(OH)_2$, is deposited.

Prepared in this way, however, the pigment is denser and does not possess the same covering power as that formed more gradually by the *Dutch process.* In this process coils of sheet lead are placed in conical vessels (Fig. 39) resting on a ledge, the bottom of the vessel containing weak acetic acid. These vessels are about 8 inches high, and a large number of them are then stacked together in layers, each layer being covered with tan or other fermenting vegetable matter. The stacks are very large, say 15 ft. square by 20 ft. high, and the heat generated by the fermentation gradually volatilizes the acetic acid and brings it into contact with the lead, and at the same time the carbon dioxide formed during the fermentation reacts with the basic acetate yielding the basic lead carbonate. The acetic acid is then free to act on a further portion of lead, and the process repeats itself until practically the whole of the lead is transformed into the "white lead."

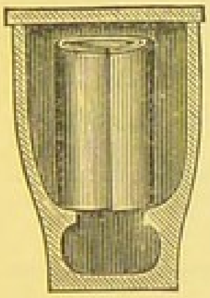


FIG. 39.

Detection and estimation.—Lead compounds when reduced on charcoal yield white malleable globules of lead. Solutions of lead salts are precipitated by sulphuretted hydrogen, the dark brown sulphide being insoluble in dilute hydrochloric acid. Sulphuric acid or soluble sulphates precipitate the sulphate of lead as a white powder almost insoluble in acids. Hydrochloric acid or soluble chlorides precipitate the lead as chloride, and this may be recognized by the fact of its being so much more freely soluble in hot water than cold. Potassium iodide gives a yellow precipitate of the iodide of lead, likewise much more soluble in hot water than cold. Lead is usually estimated in the form of lead sulphate. Traces of lead in drinking water may be estimated by observing the depth of the brown tint which is produced when sulphuretted hydrogen is passed through the sample previously acidulated with acetic acid.

CHAPTER XVII.

ARSENIC GROUP.

As, Sb, Bi.

General characters.—

The elements phosphorus, arsenic, antimony, and bismuth constitute a chemical family in which the gradation from non-metallic character in phosphorus and its compounds to the metallic character in bismuth and its compounds is well illustrated.

An examination of the group shows :—

(1) That the element phosphorus in its volatility, its electro-negative character, its vitreous nature and lustre is to be regarded as a typical non-metal, whilst bismuth, though essentially presenting the lustre and general characteristics of a metal, yet fails to possess the malleability and ductility characteristic of the more typical metals. Arsenic is more nearly identified in properties with phosphorus, and antimony with bismuth.

(2) The most important oxides have the general composition R_2O_3 and R_2O_5. In chemical character and stability these also show a gradation according to the order of the atomic weights. The oxides P_2O_3 and P_2O_5 show great stability and are both possessed of distinctly acid properties, and form with water well defined acids, and with bases stable salts, *e.g.*,

Oxides.	Acids.	Salts.
P_2O_3	$3\,H_2O\,.\,P_2O_3$ or H_3PO_3	MH_2PO_3, M_2HPO_3*
P_2O_5	$H_2O\,.\,P_2O_5$ or HPO_3	MPO_3
	$2\,H_2O\,.\,P_2O_5$ or $H_4P_2O_7$	$M_2H_2P_2O_7$, $M_4P_2O_7$
	$3\,H_2O\,.\,P_2O_5$ or H_3PO_4	MH_2PO_4, M_2HPO_4, M_3PO_4

* Only two of the three hydrogen atoms are replaceable by bases.

Very similar are derivatives of the corresponding oxides of arsenic and antimony, though the solubility of the oxides in water and the stability of the acids and salts is much smaller than in the case of phosphorus.

In the case of bismuth, the oxide Bi_2O_3 plays the part of a feeble base and combines as such with acids forming salts, such as $Bi(NO_3)_3$ $Bi_2(SO_4)_3$, etc. These, however, are not very stable and are readily decomposed by water or by the action of heat. The oxide Bi_2O_5, or rather the acid, $HBiO_3$ derived from it, has been prepared but is very unstable, and no salts are known.

(3) The tendency to form compounds with hydrogen diminishes in passing from the lower to the higher atomic weight; the trihydride of antimony has indeed not been obtained pure, and no hydride of bismuth is known. The whole of the members of the group, however, form trimethides $R(CH_3)_3$.

(4) Trichlorides are likewise known in the case of each of the elements, and pentachlorides only for antimony and bismuth. The chlorides show no great stability, and under the action of water they are transformed into oxychlorides, and by continued action the whole of the chlorine may usually be removed. The following equations will afford illustrations of such reactions.

PCl_3 by heating in oxygen = $POCl_3$
„ by the action of water = $H_3PO_3 + 3\ HCl$
(phosphorous acid)
PCl_5 „ „ moisture = $POCl_3 + 2\ HCl$
„ excess of water = $H_3PO_4 + 5\ HCl$
$AsCl_3$ „ „ „ = $AsOCl + 2\ HCl$.

$SbCl_3$ by the action of water forms $SbOCl$ and other more complex oxychlorides; by prolonged action the whole of the chlorine may be removed (as HCl) and the oxide Sb_2O_3 left as a residue.

$SbCl_5$ by adding ice-cold water = $SbOCl_3 + 2\ HCl$

By continued digestion with warm water this oxychloride passes into pyroantimonic acid ($H_4Sb_2O_7$) and ultimately into metantimonic acid ($HSbO_3$).

$BiCl_3$ by the action of water = $BiOCl + 2\ HCl$.

ARSENIC.

Occurrence.—Arsenic sometimes occurs native. More usually it is found as trioxide (arsenolite) or as sulphide (orpiment and realgar), or in combination with iron, cobalt and other metals, as arsenide (*e.g.* $FeAs_2$), or as sulpharsenide (*e.g.* mispickel, FeSAs), or as arsenates.

Metal.—By heating the oxide or sulphide in contact with carbon, or in many cases (*e. g.* arsenides) by heating the mineral in absence of oxygen, arsenic sublimes and condenses as a steel-grey powder, the vapour having a garlic odour; like antimony and bismuth it crystallizes in rhombohedra, whilst most metals assume some form of the regular system. Like phosphorus, its molecule in the state of vapour is tetratomic; at very high temperatures however it is diatomic.

The **Hydride, AsH_3.**—When solutions of arsenic compounds are introduced into a flask in which hydrogen is being generated, a highly poisonous gas is given off, consisting of the trihydride mixed with hydrogen. This gas when ignited burns in air with a dull lavender flame, forming water and arsenious oxide—

$$4\ AsH_3 + 6\ O_2 = As_4O_6 + 6\ H_2O.$$

The trihydride is not very stable and undergoes decomposition into its elements when heated. If it be passed into a solution of silver nitrate, metallic silver is precipitated and the supernatant liquid becomes acid owing to the formation of nitric and arsenious acids—

$$AsH_3 + 6\ AgNO_3 + 3\ H_2O = 6\ Ag + 6\ HNO_3 + H_3AsO_3.$$

Arsenic trihydride is also formed when a metallic arsenide is dissolved in a mineral acid.

Oxides.—There are two well-defined oxides, the arsenious oxide, As_4O_6, and arsenic oxide, As_2O_5.

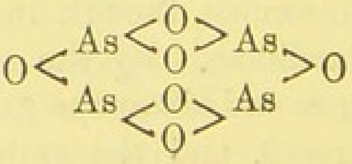
Arsenious oxide is formed when arsenical ores are roasted in air; it sublimes and condenses again in the cooler parts of the flues as a white powder. It is only slightly soluble in cold water, but more readily in hot water or dilute acids; in presence of caustic alkalies, or when boiled for some time with a solution of an alkaline carbonate, *arsenites*, M_3AsO_3, are formed, but these become readily oxidized to *arsenates,* M_3AsO_4. Arsenious oxide and the arsenites are poisonous, though in very small quantities they are employed in medicine. By the addition of an alkaline arsenite to salts of copper and silver the green arsenite of copper, $CuHAsO_3$ (Scheele's green), and the yellow arsenite of silver,

Ag_3AsO_3, are respectively obtained, and the formation of these salts as precipitates may be used for the detection of arsenic.

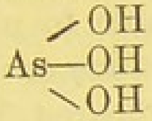
Arsenic oxide is obtained when the lower oxide is heated with nitric acid or other oxidizing agents. This oxide is readily soluble in water. Like the pentoxide of phosphorus, it forms *orthoarsenic acid*, H_3AsO_4, as above, and from this *pyroarsenic acid*, $H_4As_2O_7$, is obtained by gently heating the crystals, whilst at 200° C. *metaarsenic acid*, $HAsO_3$, is formed, and at higher temperatures the whole of the water is driven off, the anhydrous oxide, As_2O_5, being left. Orthoarsenic acid is the best known of these acids, as it forms a number of salts frequently met with, and these are similar in composition to, and isomorphous with, the corresponding phosphates. Thus we have silver arsenate, Na_3AsO_4, the brick-red precipitate obtained on adding silver nitrate to a neutral solution of an arsenate; magnesium ammonium arsenate, $MgNH_4AsO_4$, and the di-sodium salt, Na_2HAsO_4, used as a mordant. The arsenates of the alkalies are soluble in water, others being dissolved by mineral acids.

As regards the formulae of these oxides that which used to be adopted for arsenious oxide (or "white arsenic") was As_2O_3. This merely expressed the relative proportions of arsenic and oxygen as determined by the quantitative analysis of the compound and a reference to the example already given (Stannic chloride, p. 39) will show that As_4O_6, As_6O_9, etc., would have served equally well to express the proportion. As_2O_3 was adopted as being the *simplest* of these formula, it is indeed an *empirical* formula. The vapour density of the compound was found by Victor Meyer to be 13.78 times that of air at 1560° C, corresponding very nearly to 394 (Hydrogen = 1). The molecular weight of the vapour is in accordance with the formula As_4O_6 and this has therefore now been adopted as the *constitutional* formula for the compound.

Accepting arsenic in this case as a trivalent element, the oxide may be written in the graphic notation



and the corresponding arsenious acid H_3AsO_3 may be written



$$As\begin{cases}OH\\OH\\OH\end{cases}$$

though usually only two of the hydroxyl groups are replaceable by basic oxides, and so far as soluble salts are concerned it must be regarded as a *dibasic* acid.

Similarly, arsenic oxide, As_2O_5, is graphically represented by

$$\genfrac{}{}{0pt}{}{O}{O}{>}As - O - As{<}\genfrac{}{}{0pt}{}{O}{O}$$

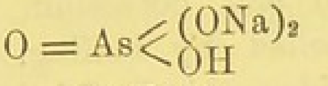
and orthoarsenic acid

$$O = As\equiv(OH)_3$$

this acid being a *tribasic* acid in which either one, two or three of the hydroxyl groups may be replaced by basic oxides in forming the arsenates thus :

$$O = As{<}\genfrac{}{}{0pt}{}{ONa}{(OH)_2}$$

NaH_2AsO_4



$$O = As{<}\genfrac{}{}{0pt}{}{(ONa)_2}{OH}$$

Na_2HAsO_4

$$O = As\equiv(ONa)_3$$

Na_3AsO_4

The phosphates follow a similar disposition.

Sulphides.—The di-sulphide As_2S_2, and the trisulphide As_2S_3, are found native as realgar and orpiment respectively ; the pentasulphide, As_2S_5, is obtained by the action of sulphuretted hydrogen on a warm solution of arsenic acid. The two latter sulphides when digested with alkaline sulphides form *thioarsenites* and *thioarsenates* respectively, salts which correspond to the arsenites and arsenates in which oxygen is replaced by sulphur, *e. g.* potassium meta-arsenite, $KAsO_2$, and the thioarsenite, $KAsS_2$, ammonium pyroarsenite, $(NH_4)_4As_2O_5$, and the thiosalt $(NH_4)_4As_2S_5$, also the thioarsenates M_3AsS_4, $M_4As_2S_7$, and $MAsS_3$, corresponding to the ortho- pyro- and meta-arsenates. These salts are decomposed on the addition of a mineral acid, the sulphide being deposited—

$$2\ Na_3AsS_4 + 6\ HCl = 6\ NaCl + As_2S_5 + 3\ H_2S.$$

These reactions are made use of in the detection and separation of arsenic.

Arsenic trichloride, $AsCl_3$, is formed by the direct combination of arsenic with chlorine, or it may be distilled over as a colourless oily liquid by heating a mixture of the trioxide and strong hydrochloric acid. In like manner the *tribromide* and *triiodide* are obtained as crystalline solids by direct union of the elements, though it is desirable to modify the violence of the reaction by dissolving the bromine or iodine in carbon bisulphide. The *trifluoride* is usually prepared by heating arsenious acid with the materials used to generate hydrofluoric acid (fluorspar and sulphuric acid). The trifluoride and trichloride are decomposed by water, forming arsenious acid as shown in the equations—

$$AsF_3 + 3\ H_2O = H_3AsO_3 + 3\ HF.$$
$$AsCl_3 + 3\ H_2O = H_3AsO_3 + 3\ HCl.$$

Detection and estimation.—Arsenic and its compounds are extremely poisonous, and their detection even when present in minute quantities is a matter of importance. If organic matter be present, this must first be decomposed by digestion with hydrochloric acid and potassium chlorate, any chlorine being completely expelled by boiling. The arsenic is then precipitated as sulphide; this is dried, mixed with potassium cyanide and heated in a bulb tube, when a black sublimate of metallic arsenic is obtained. The part of the tube bearing the deposit may then be cut off and heated in air; the arsenic is thus transformed into arsenious acid, which forms a sublimate of white octahedral crystals visible with a lens. If this be dissolved in hot water and a drop of nitrate of silver solution be added, a yellow precipitate of silver arsenite is obtained, or with ammoniacal copper sulphate a bright green precipitate of Scheele's green.

The deposit of arsenic on copper foil may be obtained by boiling it in a solution containing arsenic in presence of hydrochloric acid. This deposit may then be heated in air and treated as stated above. This is known as Reinsch's test.

The production of the hydride, AsH_3, affords a very delicate test for arsenic. An apparatus for the preparation of hydrogen is fitted with a piece of delivery tube drawn out to a jet and placed horizontally. So soon as the air has been displaced from the apparatus, the hydrogen is lighted at the jet; the lid of a porcelain tube is held in the flame, and if no black stain is produced we are satisfied that the materials used for making the hydrogen are free from arsenic. Now pour the solution to be tested down the thistle funnel; if arsenic is present, the flame assumes a lavender tint and forms a black deposit of arsenic on the porcelain lid. This is Marsh's test.

Arsenic may be estimated either in the metallic condition, or as trisulphide.

Antimony compounds under like circumstances also form a black deposit, which may be distinguished from arsenic by the fact that the latter is readily soluble in sodium hypochlorite.

ANTIMONY.

Occurrence.—The most common mineral containing antimony is stibnite or grey antimony, Sb_2S_3; the oxide, Sb_2O_3, is also known. Very frequently, antimony sulphide is associated with the sulphides of silver, copper, and lead, as thio-antimonites, *e.g.* pyrargyrite, Ag_3SbS_3 (analogous to proustite, Ag_3AsS_3, and copper bismuth blende, Cu_3BiS_3).

Metal.—This is obtained from the sulphide by heating it in covered pots with metallic iron—

$$Sb_2S_3 + 3\ Fe = 3\ FeS + 2\ Sb.$$

The excess of iron is removed by heating with charcoal and fluxes such as sodium carbonate and a further addition of the sulphide. The metal extracted in this way contains arsenic, iron, sulphur, and often lead or copper. It may be further purified by re-melting with potashes, and then on solidifying it shows fern-like markings due to crystallization and is known as "star-metal." It melts at about 450° C. and is volatile at a white heat; the fused metal expands on solidifying, and confers this property on its alloys, which are for this reason very suitable for producing sharp casts of impressions such as are required in stereotype plates. Bismuth possesses the same property. Antimony with lead and tin yields a number of useful alloys, the best known of which are type metal and Britannia metal.

The **Hydride, SbH_3,** is obtained similarly to the hydride of arsenic, with which it agrees in most of its properties. The hydride is invariably associated with free hydrogen. When heated in a tube through which the gas is passing, the black deposit of metallic antimony occurs nearer to the point at which the heat is applied than in the case of arsenic, owing to the lesser degree of volatility of the antimony. When passed through a solution of nitrate of silver, a black deposit having the composition Ag_3Sb is formed.

Oxides.—There are three well-defined oxides of antimony, antimonious oxide, Sb_2O_3, the tetroxide, Sb_2O_4, and the pentoxide, Sb_2O_5.

Antimonious oxide is formed when the metal is heated in contact with air or oxygen; prolonged heating effects further oxidation to Sb_2O_4. Metallic antimony at high temperatures also decomposes steam, forming antimonious oxide. When water is added to the trichloride of antimony, the oxychloride SbOCl is precipitated, and by prolonged digestion this is transformed into antimonious oxide.

$$SbCl_3 + H_2O = SbOCl + 2\ HCl.$$
$$2\ SbOCl + H_2O = Sb_2O_3 + 2\ HCl.$$

Similarly the pentoxide may, by the continued action of water, be transformed into $SbOCl_3$, SbO_2Cl, pyroantimonic acid, $H_4Sb_2O_7$, and ultimately antimonic acid, $HSbO_3$. Antimonious oxide is a white powder which may be vaporized without decomposition, the molecular weight of the vapour corresponding with the formula Sb_4O_6. By digestion with a solution of acid tartrate of potassium the oxide dissolves, and from the clear liquid, tartar emetic, $C_4H_4O_6.SbO.K$, may be crystallized out.

The *tetroxide* Sb_2O_4 is also a white powder obtained, as stated above, by heating the trioxide in air, and the *pentoxide* Sb_2O_5 may be prepared by treating the metal or the other oxides with nitric acid.

These oxides give rise to a numerous and complex series of acids and salts, the more important of which are the antimonic acid and the antimonates.

Pyroantimonic acid (often termed metantimonic acid), $H_4Sb_2O_7$, is formed when the white powder resulting from the action of nitric acid on the metal is heated to 100° C., and *antimonic acid*, $HSbO_3$, when the temperature is raised to 200° C. This acid is also formed on decomposing an antimonate by means of sulphuric acid;

$$KSbO_3 + H_2SO_4 = KHSO_4 + HSbO_3.$$

Potassium antimonate, $KSbO_3$ is readily prepared by adding 1 part of antimony, little by little, to 4 parts of fused potassium nitrate; on lixiviating the product, the white residue remaining is the antimonate. The sodium salt is obtained similarly; and on dissolving antimonic acid in warm ammonia, ammonium antimonate separates out on cooling. Other antimonates, being insoluble in water, may be prepared from these by precipitation methods. Sodium pyroantimonate (metantimonate), $Na_2H_2Sb_2O_7.6H_2O$, is remarkable as being the most insoluble of the sodium salts, and in this form sodium may be precipitated from solutions by the addition of the more soluble potassium metantimonate.

The **Trisulphide, Sb_2S_3**, has been already mentioned as one of the chief mineral sources of antimony. It is obtained in the hydrated form, as a deep orange-coloured precipitate, when sulphuretted hydrogen is passed through a solution of the trichloride or other antimonous compound; when heated, it is dehydrated and becomes black, corresponding then to the grey mineral sulphide, Sb_2S_3.

The *pentasulphide*, Sb_2S_5, is formed in like manner on precipitation of antimony pentachloride (tartaric acid being added to prevent precipitation of oxy-salts) or antimonic compounds with sulphuretted hydrogen. These sulphides dissolve in alkaline sulphides and form thio-salts, *e.g.* potassium thioantimonite, $KSbS_2$, and sodium thioantimonate, $Na_3SbS_4.9H_2O$; on the addition of mineral acids the thio-compounds undergo decomposition with the re-precipitation of the sulphides.

The **chlorides, $SbCl_3$** and **$SbCl_5$**, are formed when antimony is acted upon by dry chlorine, the former, if the antimony be in excess, the latter, if the chlorine be in excess. The pentachloride may be readily formed by passing chlorine through the fused trichloride. $SbCl_3$ is also obtained by the distillation of an intimate mixture of the metal or the sulphide with corrosive sublimate, $HgCl_2$.

As prepared by the above methods, the trichloride is a crystalline mass. The trichloride melts at 73° C. and boils at 223° C., but it is also frequently obtained as a viscous mass (known as *butter of antimony*) by dissolving the sulphide in concentrated hydrochloric acid and distilling the product. The pentachloride is a heavy, colourless, fuming liquid, from which crystals may be obtained by exposure to a freezing mixture of ice and salt.

Both the chlorides are decomposed by water forming oxychlorides, which are precipitated; prolonged treatment effects the removal of the whole of the chlorine leaving (in the case of the trichloride) the trioxide Sb_2O_3, and (in the case of the pentachloride) antimonic acid, $HSbO_3$.

Antimony, like arsenic, also forms the *trifluoride*, *tribromide*, and *triiodide* by direct union of the elements. They are well-crystallized substances and by the action of the water form basic oxy-salts.

Detection and estimation.—Antimony may be recognized (1) by the formation of a white precipitate when its acid solutions are diluted with water, (2) by the orange sulphide, soluble in ammonium sulphide, (3) by the production of the trihydride and decomposition thereof by heat, the metallic film being insoluble in sodium hypochlorite. It is usually estimated in the form of trisulphide, obtained by the action of sulphuretted hydrogen, and then heating in a stream of carbon dioxide until its weight is constant.

BISMUTH.

Occurrence.—Bismuth is found in the free state and also as the oxide Bi_2O_3, bismuth ochre, and more rarely as the sulphide Bi_2S_3, bismuthite.

Metal.—The metal melts at a comparatively low temperature (268° C.), and in ores containing it, may be run off from the gangue with which it is associated by the simple process of liquation. If the sulphide is worked, it must be first roasted to get rid of the sulphur and then heated in contact with charcoal and metallic iron, the bismuth being run off (as it remains molten longer) after the slag has solidified. It still contains small quantities of sulphur, arsenic, iron cobalt and other metals, but on a repetition of the liquation process it is obtained almost pure.

It is a greyish-white brittle metal which is used for alloying with lead, tin, and cadmium to produce "fusible metal," the melting point of which varies according to its composition from 61° C.

to 95° C. The larger part of the bismuth extracted is, however, used for the preparation of its salts for use in medicine.

Oxides.—The chief oxides are the yellowish trioxide, Bi_2O_3, and the orange red pentoxide, Bi_2O_5. There is also a black dioxide, Bi_2O_2, obtained on adding caustic soda in presence of stannous chloride to the solution of its salts.

The *trioxide* is obtained by heating metallic bismuth in air or may be precipitated in the hydrated condition, $Bi_2O_3.3H_2O$, by adding caustic alkalies to a solution of nitrate of bismuth.

If this oxide be suspended in a strong solution of caustic potash and exposed to a stream of chlorine, it is transformed into the *pentoxide.* This oxide readily decomposes into the trioxide and oxygen when it is heated, and, in presence of hydrochloric acid, chlorine is evolved—

$$Bi_2O_5 + 10\ HCl = 2\ BiCl_3 + 2\ Cl_2 + 5\ H_2O.$$

Bismuth trisulphide, Bi_2S_3, is formed either by fusing together bismuth and sulphur, or as a dark brown precipitate when sulphuretted hydrogen is passed through a solution of a bismuth salt. In presence of stannous chloride, the disulphide Bi_2S_2 is obtained.

The **trichloride, $BiCl_3$,** is a white substance obtained like antimony trichloride by the direct action of chlorine on bismuth or by heating together bismuth and corrosive sublimate. It may be easily fused or even volatilized; the vapour on cooling deposits it in crystals. If to the trichloride, or to a solution of the trioxide in hydrochloric acid, water be added, the oxychloride, $BiOCl$ ("pearl-white"), separates out as a white powder.

The *trifluoride, tribromide,* and *triiodide* are similarly prepared, and in presence of water these also yield precipitates of basic salts.

Bismuth nitrate, $Bi(NO_3)_3$.—Most important amongst the bismuth compounds is the *nitrate* obtained by dissolving bismuth or its trioxide in nitric acid, and the basic salts which are formed from it. If the strongly acid solution of the nitrate be *largely* diluted with water, basic nitrates are obtained of composition varying with the amount of water used or the temperature or time during which the water is allowed to act. *Magistery of bismuth, flake white,* and

Spanish white are examples of mixtures of such basic nitrates, the general nature of which may be represented by the formulæ $Bi(OH)_2NO_3$ or $BiO.NO_3.OH_2$; $Bi_2O_2(OH)NO_3$, $Bi_2O_2(NO_3)_2$. Such compounds and those resulting from action of water or heat on bismuth sulphate afford excellent illustrations of the composition of basic salts. They are salts in which part of the acid oxide has become displaced by the basic oxide or hydroxide.

Bismuth sulphate, $Bi_2(SO_4)_3$, separates out in white crystals when bismuth trioxide is dissolved in hot concentrated sulphuric acid and the solution is allowed to cool. By the action of water, the basic sulphate $Bi_2(OH)_4SO_4$ is precipitated.

$$Bi_2(SO_4)_3 + 4\ H_2O = Bi_2(OH)_4SO_4 + 2\ H_2SO_4,$$

and by heating, the basic sulphate, $Bi_2O_2SO_4$ is formed; in either case two-thirds of the acid radical is thus removed from the original salt.

Detection and estimation.—The reactions mostly used are (1) the precipitation of the sulphide in acid solution by means of sulphuretted hydrogen, (2) the reduction to the metal on charcoal, followed by solution in concentrated hydrochloric acid and precipitation of the oxychloride by addition of a large volume of water, (3) the formation of the black oxide by the action of caustic alkalies in presence of stannous chloride. Bismuth is estimated in the form of metal, oxide, or oxychloride.

APPENDIX I.

CRYSTALLIZATION AND CRYSTALLOGRAPHY.

Crystals and crystallization.—Large numbers of minerals occurring in the earth's crust are found to crystallize in definite geometrical forms. Frequently the same substance crystallizes in several different forms. Even a cursory inspection of these crystals will be sufficient to show that, whilst some of them present resemblances in type, there are others of a widely different aspect. The crystalline form or forms adopted by a certain mineral of definite composition are not arbitrary, but subject to unalterable laws. The same remarks apply to crystals produced by artificial means.

Substances in the form of powder showing no geometrical structure are termed *amorphous.* Although chemical compounds more usually come before us in this amorphous condition, they may as a rule be obtained in crystals by adopting one or other of the following expedients—

1. The substance may be heated until it fuses, and then allowed to cool slowly—*e. g.* sulphur and many metals.

2. The substance may be heated until it becomes transformed into vapour, when, on cooling, the vapour condenses, and in some cases forms crystals. This process is called *sublimation*, and may be illustrated by means of arsenious acid or benzoic acid.

3. The substance may be dissolved in water or other solvent, and then on cooling or by evaporating off part of the solvent, crystals will be obtained.

This process is known as *crystallization.* For instance, dissolve as much potassium nitrate or lead chloride as possible in say 25 c.c. of hot water, allow the solution to cool, and crystals will separate out, because these bodies are much more soluble in hot water than cold. In general, if the solution be cooled rapidly and with agitation, very small crystals will be obtained; if slowly and without disturbance, then large and well-defined crystals are obtained. If two or more salts are in solution together they will usually crystallize out in the order of their solubility, the least soluble separating out first, and the most soluble remaining to a large extent in the solution at the end (the so-called "mother-liquor").

By several repetitions of this process, it is possible to separate substances from one another more or less completely, the method being known as *fractional crystallization*. An illustration of this is afforded by a solution containing potassium chlorate, potassium chloride, and calcium chloride. The first crop of crystals will consist of potassium chlorate containing a little potassium chloride; when the bulk of the potassium chlorate has separated out, the next crop of crystals will be potassium chloride containing a little calcium chloride, and only when the solution has been boiled down to a small volume will the calcium chloride begin to crystallize as $CaCl_2.6H_2O$. Instead of water we may employ alcohol, bisulphide of carbon, benzene, and many other liquids as solvents, and these also afford crystals on evaporation, *e. g.* sulphur may be readily dissolved in bisulphide of carbon, and the solution on slow evaporation yields beautiful rhombic pyramids of sulphur.

Crystallography—The essential features of crystals.—The crystal is a regular solid of definite form, enclosed by four or more *faces*. Where two faces meet they form an *edge* which is the line of intersection of the planes of the faces. The angle between two such planes is called the *interfacial angle*. These terms may be illustrated by reference to the figure of a quartz crystal, given on p. 259 in plan and elevation.

The crystal may be regarded as a combination of the hexagonal prism and pyramid.

ON, NK, GMK, are three faces of the crystal.

MN is an edge at the intersection of the faces ON, NK.

MK „ „ „ NK, GMK.

The interfacial angle between the two prism faces ON, NK is seen by reference to the plan where EDC is the angle in question, each angle of the prism being 120°.

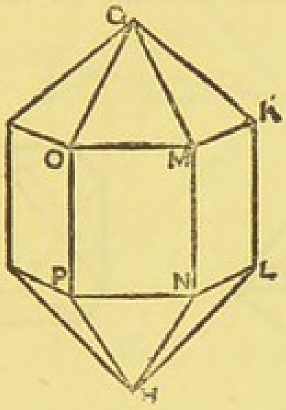


FIG. 40.

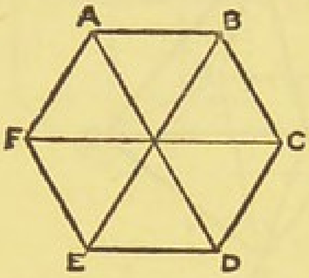


FIG. 41.

Now although it is not uncommon to find natural crystals of quartz as regular in form as the above diagram, yet in many cases variations occur which give rise to crystals wearing quite a different aspect. These variations affect the shape of the individual faces and the contour of the crystal, *but never modify the interfacial angles.* The regular hexagon, as shown above, may for instance undergo modification by the edges AB and DE being moved parallel to themselves, so as to occupy the position shown below (Fig 43).

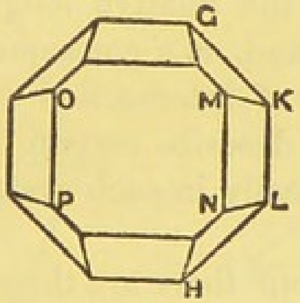


FIG. 42.

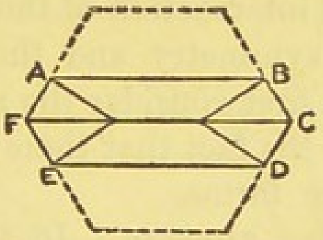


FIG. 43.

AB and DE then become *predominant* faces, but it is evident that the interfacial angles remain unaltered. The form then assumed by the crystal, in elevation, is that of Fig. 42.

Similarly the octahedron AB might not at first sight be considered to be identical with the figures alongside it. (Figs, 44 to 46.)

On measurement of the angles at which the faces intersect, however, a complete agreement will be found, and it will on inspection be evident that the first variant is due to an abnormal development of the face CBE, and the second to an abnormal development of the faces CBE and ADF. In each case, the face is developed parallel to the plane of the face of the typical octahedron, and hence the interfacial angles are unaffected.

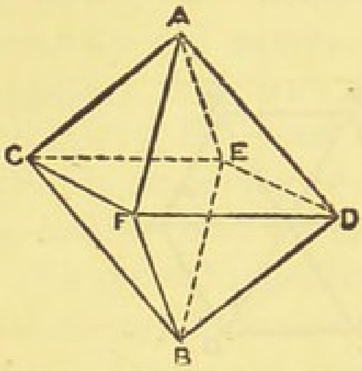


FIG. 44.

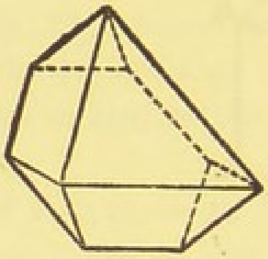


FIG. 45.

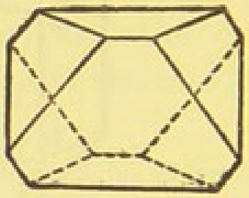


FIG. 46.

These examples will suffice to show the importance that is to be attached to the measurement of interfacial angles in determining crystals; the relations of the axes must also be taken into account and will be treated of in the description of the crystal systems.

The crystal systems.—All known crystals can be classified under one or other of six systems or families. These systems differ from one another in regard to the relative lengths and the angles of intersection of their axes, and, as a consequence of this, in their symmetry and the angles of intersection of the faces. We shall first consider the axes and describe certain forms which illustrate the fact that there are typically in each system pyramid and prism forms.

Regular system.—In this system there are three equal axes intersecting at right angles. If we draw three such axes AB, CD, EF and join their extremities, we obtain the primary pyramid form of the regular system known as the *octahedron.*

The *cube* or hexahedron is the typical prism form in this system. (Figs. 47, 48.)

Examples of substances which crystallize in these forms are—

Octahedron, alum, magnetite, cuprite.

Cube, fluorspar, common salt, potassium chloride.

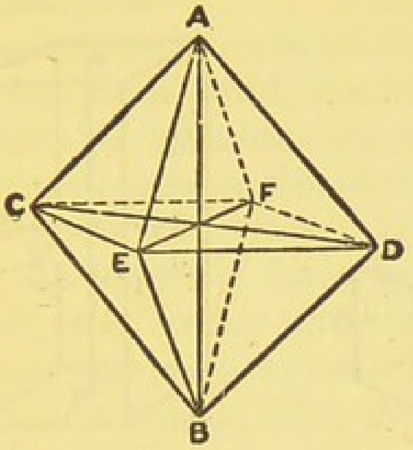


FIG. 47.

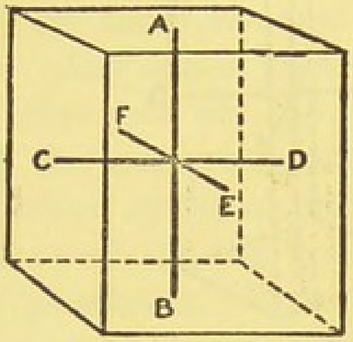


FIG. 48.

Tetragonal system.—Three axes AB, CD, EF intersecting one another at right angles as in the regular system, but two of them only are equal, the third being either shorter or longer than the other two. The typical pyramid and prism forms are shown below.

In this and the next system there are two orders of these, the first in which the horizontal axes terminate at the angles, and the second in which they intersect the edges at their middle point.

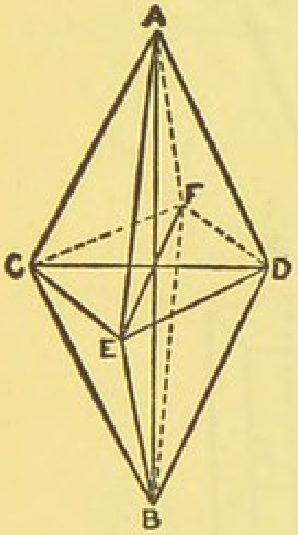


FIG. 49.

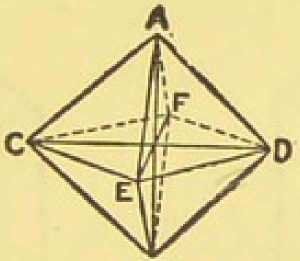


FIG. 50.

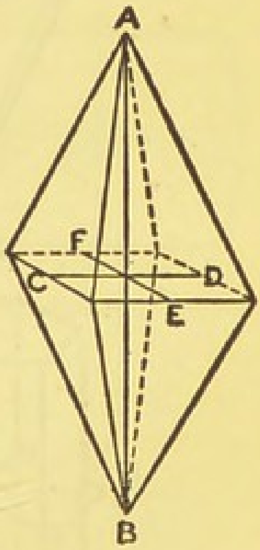
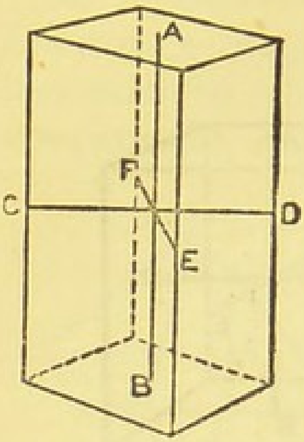


FIG. 51.

Examples.—Zircon, potassium hydrogen phosphate (KH_2PO_4) and tinstone show both prism and pyramid; ferrocyanide of potassium has the pyramid predominating.



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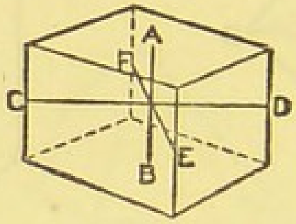

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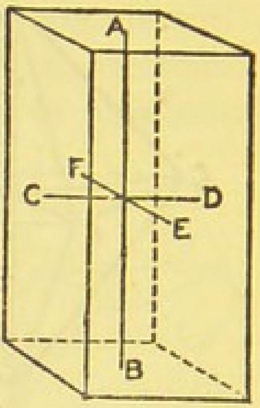


FIG. 54.

Hexagonal system.—Four axes, three equal and in the same plane intersecting one another at angles of 60°, and the fourth axis greater or less than these and at right angles to this plane.

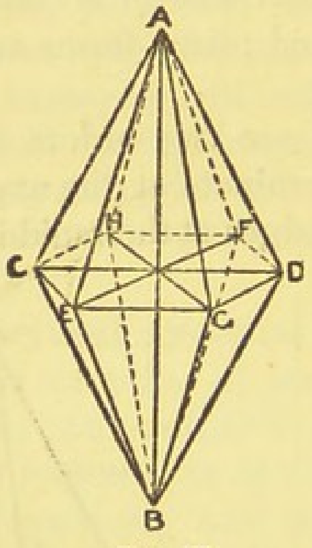
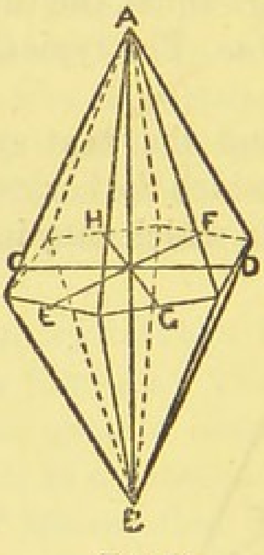


FIG. 55.



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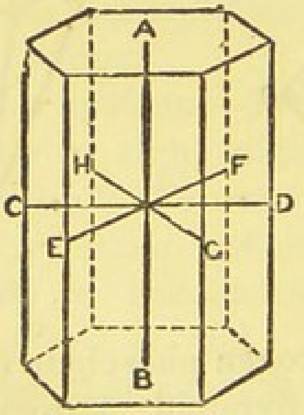

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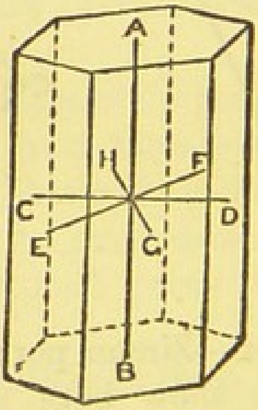


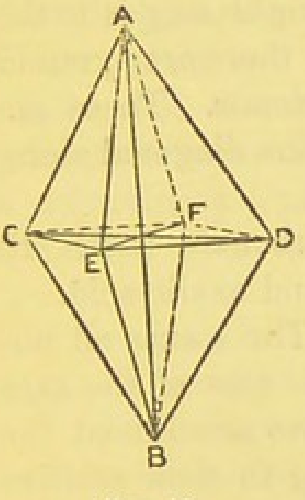
FIG. 58.

Examples.—

Pyramid forms, witherite.

Prism forms, beryl, apatite.

Rhombic system.—In this system are three unequal axes intersecting one another at right angles. Any one of these may be taken as the vertical axis and the other two are the lateral axes, the longer of these being termed the *macro-axis* and the shorter, the *brachy-axis.* As in the other systems there are pyramid and prism forms. We meet however for the first time with a new class of faces, the *domes* and *pinakoids.* Prism faces are developed not only parallel to the vertical axis, but also parallel to the lateral axes; from their position they resemble the roof of a house and are called domes. If developed parallel to the longer or macro-axis they are termed *macrodomes,* and if parallel to the shorter or brachy-axis, they are termed *brachy-domes.* See Figs. 61 and 63 below.



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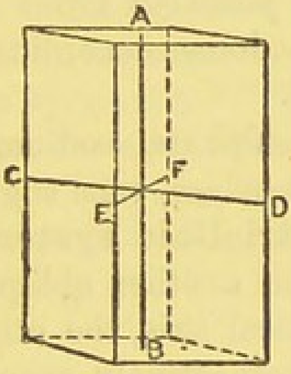

FIG. 60.

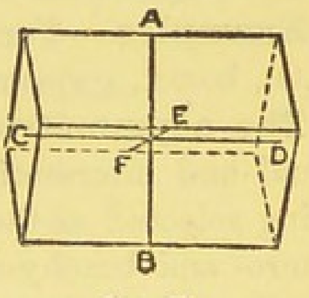

FIG 61.

FIG. 62.

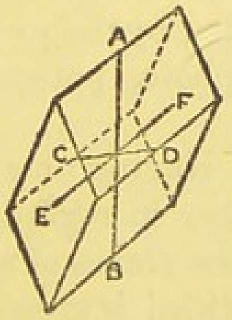

FIG. 63.

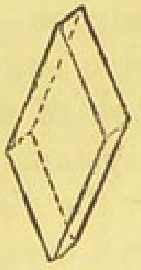

FIG. 64

These dome forms, it will be observed, are parallel to one of the lateral axes and intersect the other two axes. The pinakoid faces, on the other hand, intersect one of the lateral axes and are parallel to the other two axes, being known as *macropinakoid*, if they intersect the macro-axis, and *brachypinakoid*, if they intersect the brachy-axis. The pinakoid forms (Figs. 62 and 64) are thin tabular crystals.

Examples.—

Pyramid forms. Sulphur.

Pyramid and prism. Zinc sulphate, stibnite.

The *dome forms* are well shown in aragonite, potassium sulphate, heavy spar, magnesium ammonium phosphate, and many other substances.

The *pinakoid forms* are shown in anhydrite.

The monosymmetric or monoclinic system.—Three axes all of different lengths, two of the axes (one of these called the *klinodiagonal*) intersect one another at an oblique angle, whilst the third (called the *orthodiagonal*) axis is at right angles to the plane containing the other two. In this system there are pyramid and prism forms and also *pinakoid* forms and *domes*. These are termed orthodomes or klinodomes according to the diagonal along which they are developed.

Examples.—Ferrous sulphate, sodium carbonate (with 10 H_2O), borax, gypsum, orthoclase, cane sugar, and oxalic acid.

The asymmetric or triclinic system.—Three axes all unequal and intersecting one another obliquely. One of the axes being selected as the vertical axis, the other two are termed the macro- and brachy-axes respectively according to their relative length. The primary pyramid and prism forms are deduced as in the two previous systems and distinguished according to the axes with which they are associated by the prefixes macro and brachy.

Examples.—Copper sulphate, potassium bichromate, albite, and grape sugar.

Planes of symmetry.—Having now laid down the relations of the systems to one another in regard to their axes, we shall consider the distribution of the planes of symmetry in the crystal.

When a crystal can be divided into two similar parts by intersection along a plane surface, the substance composing the crystal is evidently symmetrically disposed on either side of the surface, which is therefore termed a *plane of symmetry;* the axis of the crystal in such a plane is known as *an axis of symmetry.* In the octahedron (Fig. 47) A E F B is such a plane of symmetry and A B an axis of symmetry; so A C B D and C E D F are planes of symmetry. Planes of symmetry also pass through the axes and the middle of each of the edges C E, E D, etc. The axes of symmetry may be further classified according to the number of planes of symmetry which pass through them. Through A B, for instance, there pass planes of symmetry A E F B, A C B D at right angles to one another, also two planes bisecting the middle of the edges C E and E D, likewise at right angles to one another and at 45° to the former planes. *Four* planes of symmetry therefore pass through A B and a like number through E F and C D. A further examination of the crystal will show that the lines joining the middle points of the edges are also axes of symmetry and that through each of these *two* planes of symmetry pass. The axes through which the greater number of planes of symmetry pass (if there are more than two such planes) are called *principal axes of symmetry* and the others *ordinary axes of symmetry.* In the regular system there are thus three principal planes of symmetry and six ordinary planes of symmetry.[1] The following table gives the number of these planes for each of the systems.

	Principal.	Ordinary.
Regular	3	6
Tetragonal	1	4
Hexagonal	1	6
Rhombic	0	3
Monosymmetric	0	1
Asymmetric	0	0

The planes of cleavage and the position of the axes along which light, heat, and electricity are most readily conducted will be found to fall in intimate relation with these axes of symmetry, and indeed much light is thrown on the physical properties and structure of crystals by considering them in relation to the axes of symmetry.

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[1] These facts are much more easily grasped by actual handling of crystals or crystal models than by the study of diagrams.

Further study of important crystal forms.—The main purpose of this chapter is to place before the student such an outline of crystallography as shall enable him to follow the remarks made upon isomorphism and to take an interest in the substances he may be expected to meet with. We must therefore somewhat extend the description, especially in those systems to which the bulk of minerals and chemical compounds belong.

The regular system.—Besides the octahedron and cube there are five other primary crystal forms belonging to this system. The *rhombic dodecahedron*, Fig. 65, having, as its name implies, 12 similar rhombic faces. The *tetrakishexahedron*, Fig. 66, with 24 similar faces each of the form of an isosceles triangle. In general habit this crystal has the appearance of a cube, on each face of which are the four faces of a square pyramid. The *triakisoctahedron*, Fig. 67, has likewise 24 triangular faces and bears the general habit of an octahedron, on each face of which are the three faces of a triangular pyramid. The *ikositetrahedron*, Fig. 68, enclosed by 24 deltoid faces. The *hexakisoctahedron*, Fig. 69, has 48 faces, each being of the form of a triangle having three unequal sides.

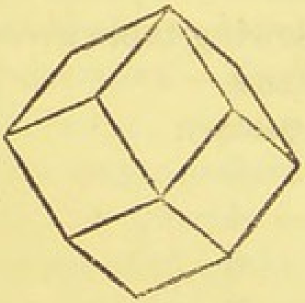
FIG. 65.

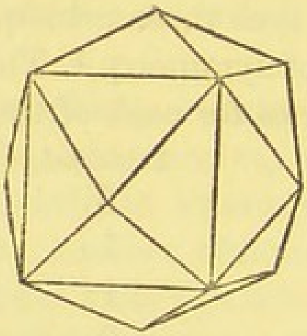
FIG. 66.

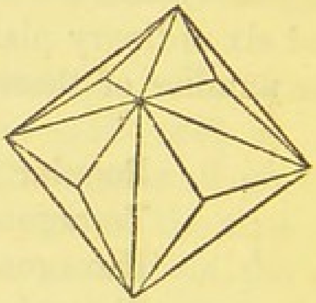
FIG. 67.

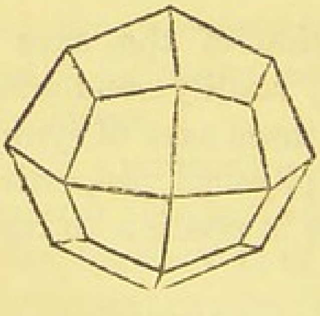
FIG. 68.

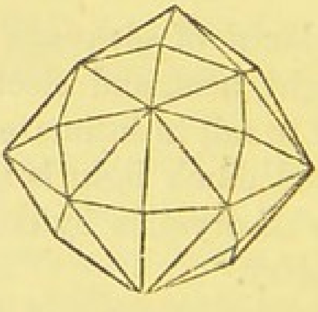
FIG. 69.

We have already spoken of the importance of the faces and interfacial angles as a guide to the recognition of a crystal. Notwithstanding the apparently complex nature of the above forms, it will be found that an expression connecting the faces and the axes for one of the faces, answers equally for all the faces. The crystal is fully described when an expression has been obtained which gives the intercepts of any one face on the axes of the crystal. These intercepts are—*a*, if they are the same length as the axes of the crystal; *ma* or *na*, if they are longer than the axes; ∞ *a*, if the plane of the face is parallel to the axis, and therefore does not cut it.

Each face of the *octahedron* manifestly meets the extremities of the axes in the quadrant in which the face lies. Its intercepts are therefore a : a : a.

Each face of the *cube* is parallel to two of the axes, and cuts the other at the distance *a* from the centre. Its intercepts are therefore a : ∞ a : ∞ a.

Each face of the *rhombic dodecahedron* will be seen to meet two of the axes at their extremities, and to lie in a plane parallel to the third. Its intercepts are therefore a : a : ∞ a.

So the intercepts of the *tetrakishexahedron* are a : ma : ∞ a
,, *triakisoctahedron* ,, a : a : ma
,, *ikositetrahedron* ,, a : ma : ma
,, *hexakisoctahedron* ,, a : na : ma

The values *m* and *n* are multiples or fractions made up of small numbers, such as 2, 3, $\frac{3}{2}$, $\frac{4}{3}$; and beyond the variations which such differences of value admit of, no other forms than those given are possible.

Combination forms.—Very frequent, however, in the mineral kingdom are combination forms in which two or more of these types occur in the same crystal. Figs. 70 and 71 show the combination of the cube and octahedron, the cube being predominant in the first, and the octahedron in the second.

Fig. 72 is a cube whose edges are modified by combination with another form, which, on investigating the relation of the faces to their intercepts on the axes, will give the expression—a : a : ∞ a; that is the rhombic dodecahedron.

However complex these forms may appear, they present no difficulty so soon as the principle of referring the faces to their intercepts on the axes is understood.

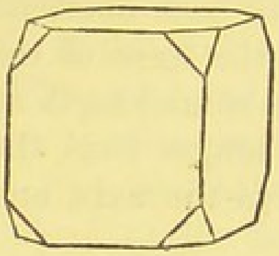

FIG. 70.

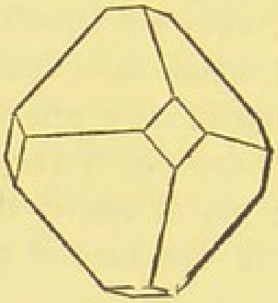

FIG. 71.

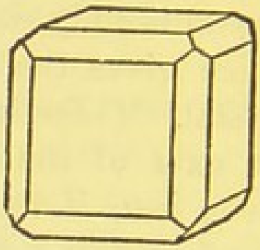

FIG. 72.

Hemihedral forms.—In the other systems, the complexity of typical forms is not so great as it is in the regular system; additional types, however, arise in all the systems through the occurrence of *hemihedral* crystals, forms in which half the faces are suppressed.[1] The hemihedral forms of the regular and rhombic systems are so common that they cannot be overlooked even in this brief outline.

Thus, if in the octahedron, alternate faces alone are developed, we get a figure enclosed by four faces instead of eight, and called the *tetrahedron;* this is illustrated in Figs. 73 and 74.

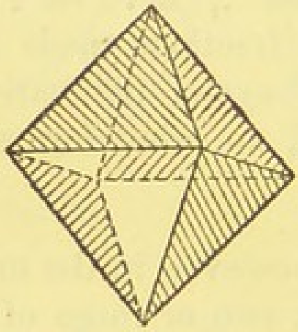

FIG. 73.

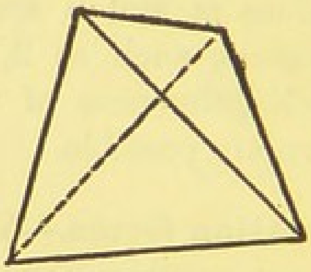

FIG. 74.

Examples.—Sodium sulpho antimonate, boracite.

Even more important are the hemihedral forms in the hexagonal system. Here from the hexagonal pyramid, by the development

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[1] In some instances one-fourth of the faces are developed, and in this case we have what are known as *tetartohedral* crystals.

of alternate faces, we obtain the *rhombohedron*, a form of very frequent occurrence. This is shown in Figs. 75, 76, 77. The positive and negative forms of the rhombohedron arise according to which set of the alternate faces of the pyramid is developed. Also from the dihexagonal pyramid, Fig. 78 (obtained by the combination of the hexagonal pyramids of the 1st and 2nd order), with 24 faces by the disappearance of alternate pairs of faces, the *scalenohedron*, Fig. 79, is produced, and by disappearance of alternate faces, the *trapezohedron*, Figs. 80, 81, as shown in the figures below. These forms are also very common in the mineral kingdom.

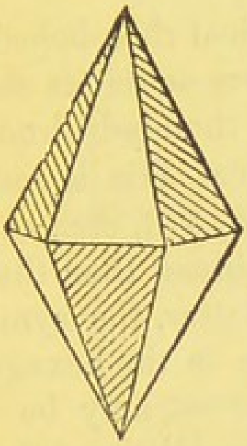
FIG. 75.

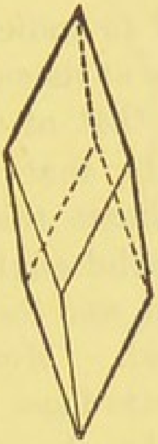
FIG. 76.

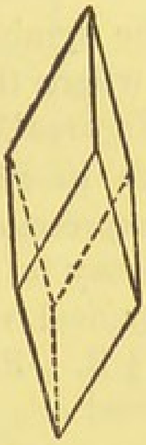
FIG. 77.

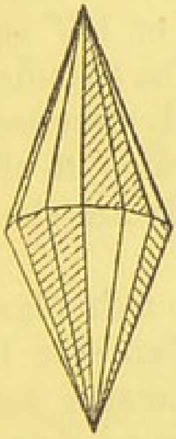
FIG 78.

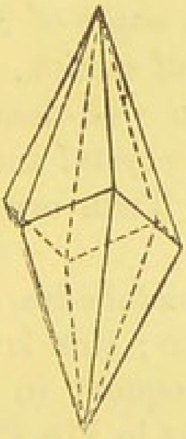
FIG. 79.

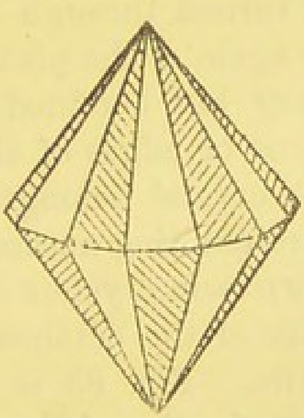
FIG. 80.

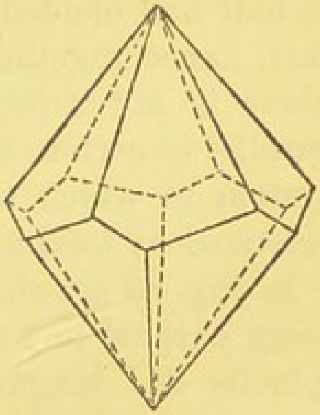
FIG. 81.

Examples.—

Scalenohedra, Calcite.

Trapezohedra, Quartz.

Rhombohedra, Hæmatite, calcite, calamine, potassium and sodium nitrates, magnesite, witherite, strontianite.

The symbol R is used to indicate the typical rhombohedron, and where the solid angle at its summit is more acute (as shown in Figures 76, 77) than that of the typical rhombohedron (as shown in Fig. 6, page 21), that is, the vertical axis is longer, the expression used to indicate this is, 2 R, 3 R, 4 R, etc., as the case may be; where the solid angle is more obtuse than that of the typical rhombohedron, and the form is flatter, the symbols $\frac{1}{2}$ R, $\frac{1}{4}$ R, $\frac{1}{8}$ R, etc., are used. Moreover, since in the hexagonal pyramid one set of alternate faces or the other set may be predominant, the faces of the rhombohedra will lie in different planes (see Figures 76, 77), these are distinguished as positive and negative rhombohedra; the symbols $+$ R, $-$ R, $+\frac{1}{4}$ R, or $-$ 3 R, and the like, are used to represent this. Similarly there are positive and negative scalenohedra and trapezohedra.

Twin crystals.—It often happens that in crystal masses, two or more individual crystals grow in contact so that either is incomplete, the crystals having a common plane (the twinning plane) at which they are in contact. In such a case the directions of the principal axes of the two crystals are not in the same line. Frequently it appears as though an ordinary crystal had been cut in half and one half turned through an angle of 90° or 180° and then joined together again at the plane of section. The twinning plane is not arbitrary but confined to well-defined directions parallel to certain faces or edges of the crystal according to the system to which the crystal belongs. Twin crystals are characterized by having re-entering angles.

In Fig. 82 are shown twin crystals of octahedra, the twin plane being parallel to a face of the octahedron; this is often seen in spinelle and magnetite. Fig. 83 is frequent in fluorspar and shows two cubes, the twin plane being, as in Fig. 82, parallel to a face of the octahedron. In Fig. 84 is an example of a form of twin common in the tetragonal system, and occurring in tinstone and rutile; and in Fig. 85 is the so-called arrowhead twin characteristic of gypsum, the system being monoclinic.

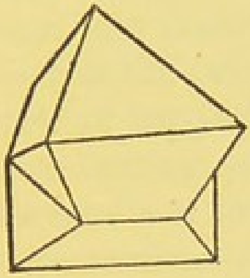

FIG. 82.

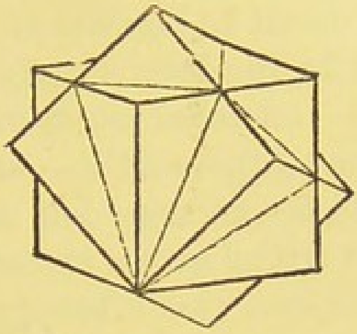

FIG. 83.

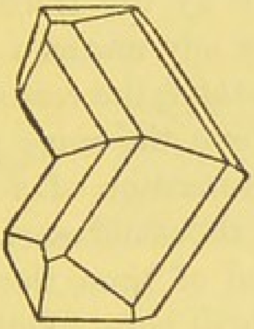

FIG. 84.

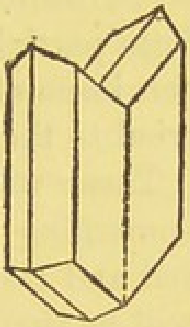

Fig. 85.

APPENDIX II.

SPECTRUM ANALYSIS.

SOUND is transmitted through the air by the transference of impulses from particle to particle. If by any means a succession of forty such impulses are set up in a second, the record of these will be carried to the ear and produce there the same number of impulses. These will give rise to the sensation of a very deep note. If something approaching forty thousand such impulses be originated and transmitted in a second of time, the sensation produced will be that of an extremely shrill note. Outside these limits the ear fails as a means of recording impulses.

We shall now consider an order of vibration much more rapid than that which we appreciate as sound. If a platinum wire be heated[1] to about 600° C. it may be seen to glow with a dull red heat, just visible in a dark room, and as the temperature rises the dull redness passes to a brighter red and ultimately, at about 1500° C., to a white heat. These appearances are due to the vibration of the particles of the platinum. They are, however, very much more numerous than those already referred to, amounting for dull redness to some 500 billions per second, and at white heat approaching 700 billions per second.

They differ also in their mode of transmission and reception. The sensation of light to which they give rise on the retina is carried through the medium of the ether, a substance of vastly greater tenuity than the gaseous atmosphere. This medium per-

---

[1] This may conveniently be done by passing the current from two Grove's cells through a length of *thin* platinum wire.

vades space and the interspaces between the particles which we recognize as matter, whether it be solid, liquid, or gaseous. The difference extends also to the rapidity of transmission, for whilst sound impulses are carried forward at the rate of about 1100 feet per second, the transmission through the medium of the ether takes place at the rate of 186,000 miles per second.

Spectra of incandescent solids.—White light, such as we observe on heating solid substances and such as we see in the flame of a candle or the rays of the sun, is set up by the vibrations of immense numbers of solid particles, and it may easily be shown that these are not all vibrating at the same rate. This is proved in the following manner. A prism, A B C, of a transparent substance, such as glass, is interposed between a narrow beam of white light, L, and the screen, D E, on which it is ultimately received. There will appear on D E a band of light (called a *spectrum*) showing every variety of colour from red (at R) to violet (at V). It thus appears that in passing through the prism the light is refracted, and in different degrees, the red to the least extent and the violet to the greatest extent. The red rays are therefore frequently spoken of as the less refrangible rays and the violet rays as the more refrangible. A solid body heated to dull redness sends out chiefly vibrations of the red kind, and if examined by the interposition of a prism, the band of light received on the screen will be shorter and differ from that given by a body at white heat by the absence of the blue and violet rays. All solid bodies when heated to a sufficiently high temperature give rise to white light, which gives a continuous spectrum on the interposition of a glass prism.

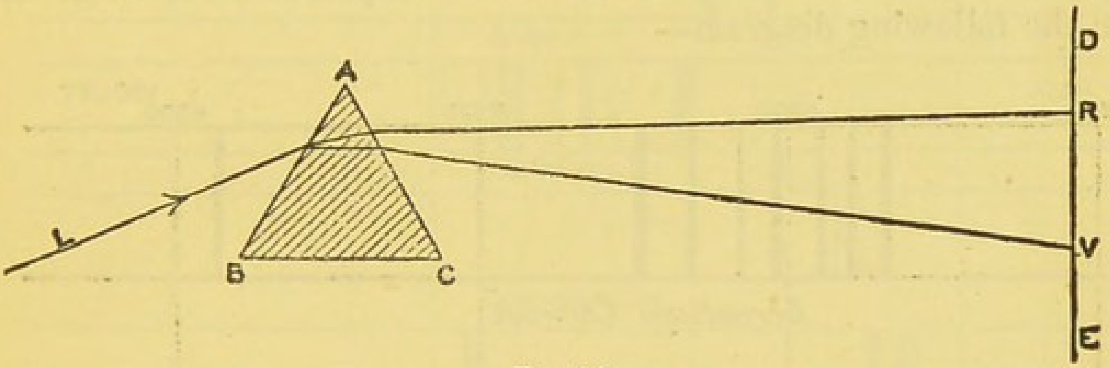

FIG. 86.

Spectra of gases or vapours.—If a small quantity of a substance such as strontium chloride or cupric chloride be brought into the non-luminous flame of a Bunsen burner, the body will, owing to the high temperature, be vaporized and the flame coloured, crimson in the case of the strontium chloride and green in the case of the cupric chloride. Should we now examine this light by means of a prism, we shall observe that it does not show every variety of colour, nor does it show merely the red or green part respectively. It is, indeed, quite distinct in its nature from the spectram already described, and consists of a number of lines (images of the slit through which the light is admitted) whose positions are for the same substance invariable. The positions of the chief lines for strontium chloride and cupric chloride are given in the following diagram—

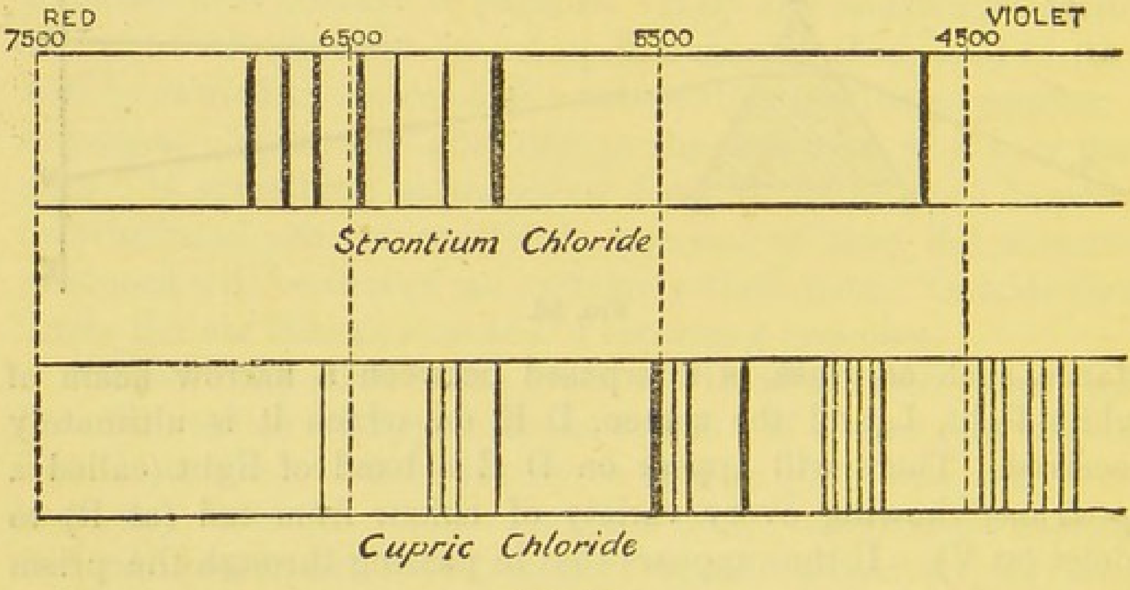

FIG. 87.

The numbers supply the scale of wave-length in terms of "tenth metres," *i. e.* $\frac{1 \text{ metre}}{10,000,000,000}$ or in ten millionths of a millimetre.

It is also found that each element when vaporized in the flame gives one or more (often a large number) of such lines, each and all characteristic for the given element, so that no two lines occupy the same position. In the following diagram the position and relative strength of the lines for a number of elements are represented. The spectra for Na, Li, K, Ca, and Tl, are given

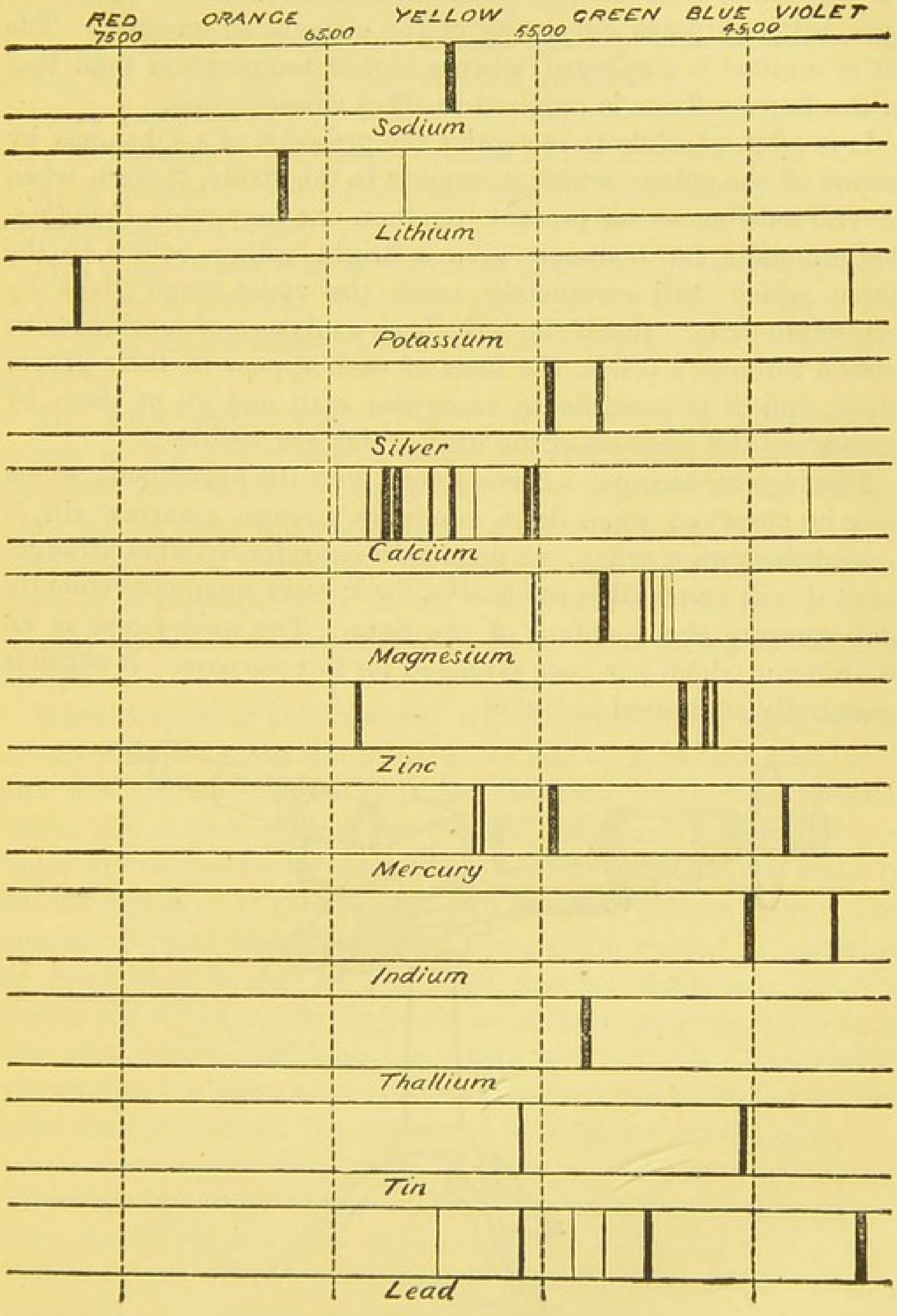
RED
ORANGE
YELLOW
GREEN
BLUE
VIOLET
7500
6500
5500
4500
Sodium
Lithium
Potassium
Silver
Calcium
Magnesium
Zinc
Mercury
Indium
Thallium
Tin
Lead

FIG. 88.

above as observed when a volatile salt is introduced into the Bunsen flame; the others, when induction sparks are caused to pass between poles consisting of the element in question. The latter method is employed when a higher temperature than that of the Bunsen flame is required to effect volatilization.

It is often possible to recognize the presence of a substance by means of the colour which it imparts to the flame, though when several substances are present together, one may mask the other. Sodium salts, for instance, give a bright yellow colour to the flame which will completely mask the violet tinge given by potassium salts. But if the light from a mixture of substances be passed through a prism, the lines of each appear in their proper place, and it is possible to recognize each and all of them by measuring the position of the lines which are visible.

The spectroscope.—Having dealt with the phenomena which may be observed when light, admitted through a narrow slit, is passed through a prism, we must now consider by what arrangement it will be possible to observe the spectra more conveniently and measure the positions of the lines. The *spectroscope* is an instrument which has been arranged for this purpose. It consists essentially as figured below of

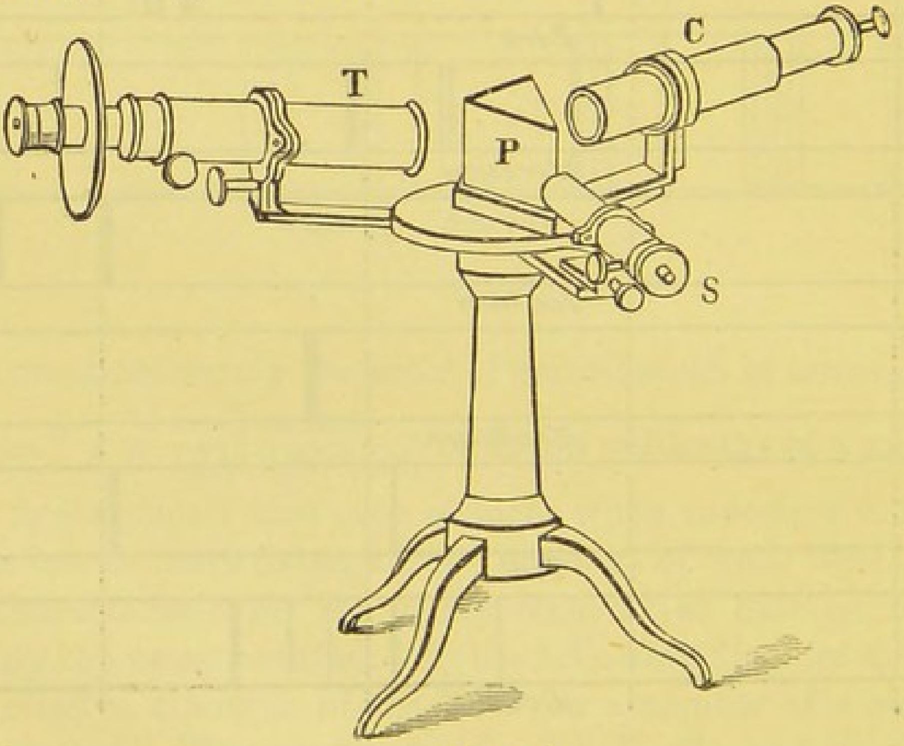

FIG. 89

(1) A tube provided with a narrow slit by which the light is introduced, and termed the collimator tube (C).

(2) A glass prism (P), or several glass prisms arranged in series, for giving greater dispersion of the light.

(3) A telescope (T), by which the image or images of the slit may be brought into focus and rendered distinctly visible.

(4) A means of determining the relative positions of the lines by reference to a scale.

This latter object may be achieved by a scale of equal divisions at S, which is reflected from the surface of the glass prism along the axis of the telescope so that its image appears adjacent to the spectrum.

The solar spectrum.—If the light of the sun be examined by means of the spectroscope, using a narrow slit, a continuous spectrum will be seen crossed by a large number of *dark* lines, some well defined and easily seen, others extremely thin and only visible by careful focussing. In position, and in distinctness also, these lines correspond in almost every case to the bright lines already spoken of as obtained from one or other of the elementary bodies.

Before inquiring into the full significance of the appearances observed in the solar spectrum, let us ask why, in this case, dark and not bright lines of light are obtained. Let us suppose a white hot surface giving out intense light and in front of it a layer of comparatively cool vapour, of say sodium, sufficiently heated however to give out its own peculiar yellow light. The amount of light proceeding from the sodium vapour is relatively so small that it may be neglected, and we shall only have to regard the effect which the presence of the vapour may have upon the rays proceeding from the white hot surface. Experiment shows that the ether waves proceeding from the white hot surface pass readily through the vapour of sodium, *except the vibrations whose wave-length corresponds to those of the screen of vapour.* These are in a large measure absorbed or quenched in that screen. Now we have seen that sodium vapour emits light of a pure yellow colour whose wave-length is approximately 5900. If then the white light which has passed through such a layer of sodium vapour be examined in the spectroscope it will be found to be deprived or partially deprived of the rays whose wave-length is 5900. At that part of the spectrum a dark space or line will appear corresponding exactly in position with the sodium line. In the same way if the layer of vapour contains also lithium there will be an absorption at wave-length 6700 corresponding to the position of the lithium line, and so on for each substance whose vapour is present. We shall under such circumstances have the spectrum of white light interspersed with dark lines corresponding to all the substances so present, in the layer of vapour. In the case of the sun, the white hot radiating surface is the body of the sun itself, the *photosphere*, and the absorbing layer is an envelope or atmosphere of the cooler vapours emitted from the body of the sun, termed the *chromosphere.* This is the explanation, due to Kirchhoff, of the existence of dark lines in the sun's spectrum. The following simple diagram will illustrate these remarks, the shaded part being the section of the photosphere and the dotted annular portion that of the chromosphere.

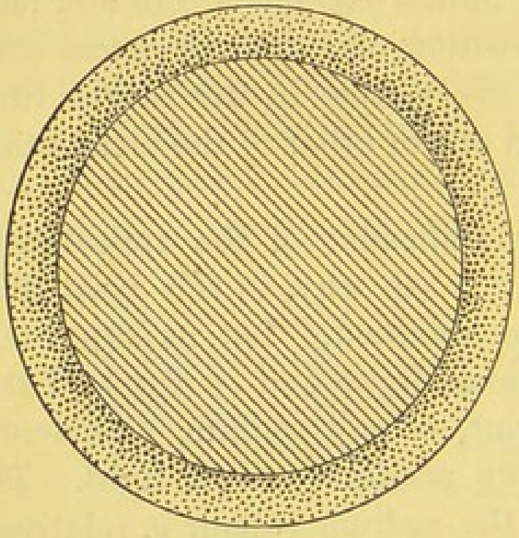

FIG. 90.

By special arrangements or during a total eclipse, when the body of the sun (the photosphere) is just hidden by the interposition of the moon, it is possible to examine the light which proceeds from the chromosphere alone, and under these circumstances the glowing vapours which exist there are actually found to give rise to bright lines, precisely as the glowing vapours in the Bunsen flame do. Extended observation has indeed confirmed in every way the explanation given by Kirchhoff. The dark lines therefore in the sun's spectrum are just as much to be depended on as evidence of the presence of various elements in the sun as the bright lines are in relation to spectra as seen in the laboratory. The absolute coincidence in position with these convinces us of the existence in the sun of a large number of the elements identical with those which form part of the earth's crust.

The haloid elements, and also nitrogen, oxygen, gold, mercury, and a few other elements, have as yet given no sufficient indication of their presence in the sun.

Spectra of the stars, nebulæ, and comets.—Observations on the fixed stars furnish evidence of a similar composition, whilst the light from nebulæ gives spectra showing the lines of hydrogen, helium, carbon, magnesium, calcium, and iron, and in comets the presence of hydrogen and hydrocarbons has been recognized.

Absorption spectra.—There are many solid bodies which show a characteristic colour by light reflected from their surfaces, and in thin films or plates they appear coloured by transmitted light. Thus gold, when burnished, is yellow by reflected light, but if a thin film of gold (gold-leaf) be examined by transmitted light it is of a dull green colour. Also if to a very dilute solution of chloride of gold, ferrous sulphate be added, the liquid will appear purple by transmitted light, whilst the light reflected from the surface of the fine particles of gold in suspension is of a rich brown colour.

Solutions of salts in many cases appear coloured by transmitted light; a solution of sulphate of copper is blue, one of potassium permanganate is a rose-purple, potassium chromate is yellow. Such phenomena are in all cases due to selective absorption. A body whose surface reflects all the rays indiscriminately appears white; the yellow colour of gold is due to the fact that most of the red, green, blue, and violet rays are absorbed, the predominant reflected rays being yellow. Similarly copper sulphate is of a blue colour because in it the rays of other colours contained in white light are absorbed in the solution and only the blue rays transmitted. This absorption can easily be rendered evident by placing before the slit of the spectroscope a solution of ammonio-sulphate of copper,[1] when it will be seen that the less refrangible end of the spectrum is cut off. So, if bichromate of potash be used, the more refrangible end of the spectrum is cut off, and by placing before the slit, cells containing each of these solutions, the whole of the light may be cut off.

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[1] Prepared by adding ammonia to a solution of sulphate of copper until the precipitate which first forms is entirely redissolved.

Coloured solutions as a rule absorb the rays in a particular region of the spectrum, as in the case of the salts already referred to, but in some cases the absorption is of a more complex character. Thus potassium permanganate gives a number of absorption bands extending over the yellow, green, and blue region of the spectrum, as shown in the figure below.

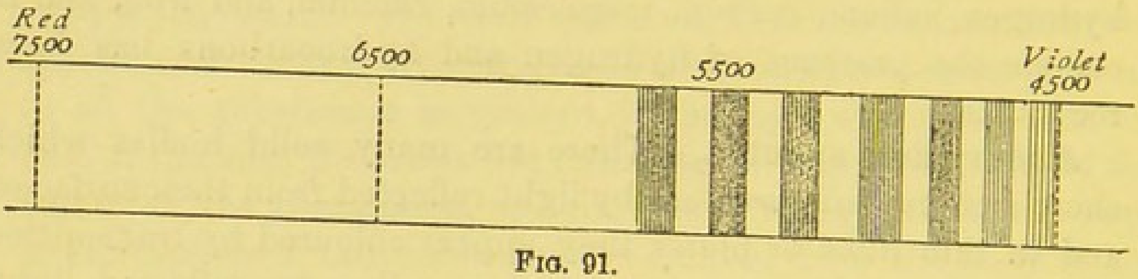

FIG. 91.

As further examples of absorption spectra we may quote (1) the green colouring matter (chlorophyll) of plants dissolved in ether, and (2) a solution of didymium chloride, which has only a faint rose tint.

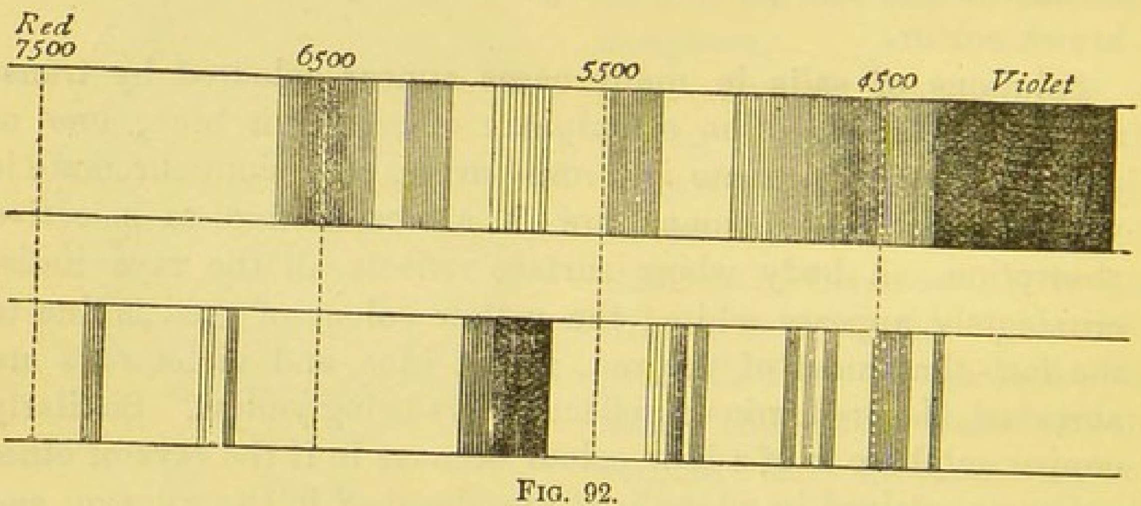

FIG. 92.

Many other similar examples are presented by dyes and by fluids derived from organisms, *e. g.* blood. The positions of these bands is just as definite and characteristic as the lines are for flame spectra, and the spectroscope may therefore be used for the purpose of recognizing such bodies in solution.

Spectra of gases.—In order to obtain the spectra of gases, induction sparks are passed through a tube of the gas in question partially exhausted. By this means the gas becomes incandescent, and the light when examined by the spectroscope shows either a series of bright bands, or of lines, whose position is characteristic for each gas, or a continuous spectrum, according to the pressure under which the gas is confined. At the lowest pressure bands are seen, which with increasing pressure give place to lines and ultimately to a continuous band of light, corresponding with the pure spectrum. The character of the lines varies also with the temperature under which the gas or vapour is observed, and in many cases, when a higher temperature is employed, new lines appear in the spectrum.

These circumstances afford some means of judging of the conditions which obtain in the heavenly bodies. For instance, sodium in the Bunsen flame gives rise to one (really two, very close together) well-defined yellow line, but at higher temperatures, three other pairs of lines make their appearance ; in the sun the whole of these lines are visible.

APPENDIX III.

CHEMICAL CALCULATIONS.

I.—The relations between weight and volume of gases.

We have seen (Chapter I.) that the densities of gases are proportional to their molecular weights. In order to express the weight of any gas it is convenient to remember as the basis of calculation that 1 *litre of hydrogen at the standard temperature* (*0° C.*) *and pressure* (*760 m.m. of mercury*) *is* 0·0899 *grammes*, or that 11·12 litres of hydrogen weigh one gramme.

If then we desire to ascertain the weight of any other gas under like conditions, we commence by expressing in chemical symbols the molecule of the gas thus—

The molecule of hydrogen is expressed by H_2 (2)
of nitrogen by N_2 (28)
of chlorine by Cl_2 (71)
of phosphorus by P_4 (124)
of hydrochloric acid by HCl (36·5)
of nitric oxide by NO (30)
of sulphuretted hydrogen by H_2S (34)
of oxygen by O_2 (32)
of ozone by O_3 (48)
of water vapour by H_2O (18)
of carbon dioxide by CO_2 (44)
of sulphur dioxide by SO_2 (64)
of ammonia by NH_3 (17)

The relative weights are, then, those stated in parenthesis after the symbol in the above list, as derived from the respective atomic weights.

Thus the weight of a litre of nitrogen is 14 times that of a litre of hydrogen or (0·0899 × 14) grammes; a litre of carbon dioxide weighs (0·0899 × 22) grammes; a litre of sulphuretted hydrogen weighs (0·0899 × 17) grammes.

The alternative method of expressing the same facts is perhaps more readily applied in chemical calculations, viz. that 11·12 litres of hydrogen weigh 1 gramme or 22·24 litres (usually stated as 22·4) of hydrogen weigh 2 grammes, the same number of grammes as that used for expressing the molecular weight. In this form the statement is quite general, that the molecular weight being *m*, 22·24 litres of any gas whatever weigh *m* grammes.

22·24 litres of nitrogen weigh 28 grammes.
22·24 „ „ oxygen „ 32 „
22·24 „ „ chlorine „ 71 „
22·24 „ „ sulphur dioxide „ 64 „
22·24 „ „ ammonia „ 17 „

It is convenient to remember both forms of the expression, as one or the other is more readily adapted for the purpose of calculation according to the terms which are given. For instance, if it be desired to calculate the weight of a certain volume of a gas, the former expression lends itself more readily for the purpose—as in the following example—

(1) Required the weight of 100 c.c. of carbon dioxide at 0° C. and 760 m.m. pressure—

1000 c.c. (1 litre) of hydrogen weigh 0·0899 grammes.
„ „ carbon dioxide „ 1·9778 „
100 cubic centimetres of „ „ „ 0·19778 „

Should the weight of the gas be given, and its volume is to be determined, the second form of expression is more easily applied.

(2) Required the volume occupied by 0·5 gramme of ammonia at 0° C. and 760 m.m. pressure—

17 grammes of ammonia occupy 22·24 litres.
1 „ „ „ 1·308 „
0·5 „ „ „ 0·654 „

It is useful also to bear in mind that air is 14·435 times as heavy as hydrogen, since frequently the densities of vapours as actually determined by experiment are stated in terms of air as unit.

Thus the density of sulphur dioxide is found by experiment to be 2·247, air being the unit.

The density compared with hydrogen is therefore 2·247 × 14·435, or 32·43, a value agreeing well with that deduced from the accepted composition of this gas.

II.—Correction for temperature and pressure.

We shall first consider the influence of variations of *temperature* on the volume of a gas, and consequently on the weight of a given volume.

We have seen (Chap. I.) that a gas at 0° C. expands $\frac{1}{273}$ of its volume for each increment of one degree Centigrade in temperature. The more general form of expression, viz. that the volume of the gas is proportional to the absolute temperature (see p. 3), will be found the most useful, as a few examples will show. In order to make the calculation it is in the first place necessary to convert the temperatures as ordinarily stated into absolute temperatures.

(3) A litre of gas is measured at 0° C.; what volume will it occupy at − 20° C., and what at 50° C.?

$$0° \text{ C.} = 273° \text{ absolute.}$$
$$-\ 20° \text{ C.} = 253° \quad ,,$$
$$+\ 50° \text{ C.} = 323° \quad ,,$$

$$\text{Volume required is at } -\ 20° \text{ C.} \quad 1 \text{ litre} \times \frac{253}{273} = 926{\cdot}8 \text{ c.c.}$$

$$,, \quad ,, \quad ,, \quad +\ 50° \text{ C.} \quad 1 \text{ litre} \times \frac{323}{273} = 1183{\cdot}2 \text{ c.c.}$$

(4) The volume of a gas measured at 10° C. is found to be 150 c.c.; what volume would it occupy at the standard temperature (0° C.)?

$$10° \text{ C.} = 283° \text{ absolute.}$$

$$\text{Volume required is at } 0° \text{ C.} \qquad 150 \times \frac{273}{283} = 144{\cdot}7 \text{ c.c.}$$

(5) The volume of a gas measured at 15° C. is found to be

250 c.c.; what volume would it occupy at − 15° C. and at 57° C. respectively?

15° C. = 288° absolute.
− 15° C. = 258° „
+ 57° C. = 330° „

$$\text{Volume required at } -15^\circ\text{ C.} = 250 \times \frac{258}{288} = 224{\cdot}0 \text{ c.c.}$$

$$\text{„ „ „ } +57^\circ\text{ C.} = 250 \times \frac{330}{288} = 286{\cdot}5 \text{ c.c.}$$

And now let us consider the effect of variation in *pressure*. According to Boyle's Law (see p. 5), the volume of a gas is inversely proportional to the pressure to which it is subjected when the temperature is constant.

(6) A gas measured at standard atmospheric pressure (760 m.m.) is found to occupy 1·5 litres; what volume will it occupy at 1,000 m.m. and at 100 m.m. pressure?

$$\text{Required volume at 1,000 m.m. is } 1{,}500 \times \frac{760}{1{,}000} = 1{,}140 \text{ c.c.}$$

$$\text{„ „ „ 100 m.m. is } 1{,}500 \times \frac{760}{100} = 11{,}400 \text{ c.c.}$$

(7) The volume of a gas at 500 m.m. pressure is found to be 250 c.c.; what would it measure under 5 atmospheres pressure?

5 atmospheres = (760 × 5) m.m. = 3,800 m.m.

$$\text{Required volume at 5 atmos.} = 250 \times \frac{500}{3{,}800} = 32{\cdot}9 \text{ c.c.}$$

Finally, an example is given of the allowance for both temperature and pressure in the same expression.

(8) A gas occupies 190 c.c. at 13° C. and 740 m.m. pressure; what volume would it occupy at standard temperature and pressure (0° C. and 760 m.m.), and what at − 130° C. and 780 m.m. pressure?

13° C. = 286° absolute.
0° C. = 273° „

$$\text{Volume at } 0^\circ\text{ C. and 760 m.m.} = 190 \times \frac{273 \times 740}{286 \times 760} = 176{\cdot}6 \text{ c.c.}$$

− 130° C. = 143 absolute.

$$\text{Volume at } -130^\circ\text{ C. and 780 m.m.} = 190 \times \frac{143 \times 740}{286 \times 780} = 90{\cdot}1 \text{ c.c.}$$

III.—The relation between weight and volume of liquids and solids.

The specific gravity of liquids is expressed in terms of pure water at 15° C. as unit. The following table shows that the specific gravity of water varies at different temperatures, water at 4° being taken as 1.

Specific gravity of water at 0° = 0·99987
" " " 2° = 0·99997
" " " 4° = 1·00000
" " " 10° = 0·99975
" " " 15° = 0·99916
" " " 20° = 0·99826
" " " 25° = 0·99712

In ascertaining the density of a liquid by comparison with water it is more convenient to make the determination at ordinary temperatures, and hence it is usual to adopt the specific gravity of water at 15° C. as the basis of comparison.

When we say that the specific gravity of a liquid is 1·8 we mean that it is heavier than water in the proportion 1·8 : 1; if therefore 1 c.c. of water weighs 1 gramme, 1 c.c. of such a liquid will weigh 1·8 grammes.[1] The following examples will show how specific gravity of liquids enters into chemical problems.

(9) What is the weight of 100 c.c. of sulphuric acid of sp. gr. 1·84?

100 c.c. of water weigh 100 grammes.
" " sulphuric acid of the density given " 184 "

(10) Hydrochloric acid of sp. gr. 1·112 contains 21 per cent. by weight of gaseous hydrochloric acid; find the volume of hydrochloric acid gas in 10 c.c. of such acid.

By the method used in the previous problem 10 c.c. of hydrochloric acid will weigh 11·12 grammes.

$\frac{11·12 \times 21}{100} = 2·3352$ grammes, the weight of gaseous hydrochloric acid contained in it.

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[1] This is not strictly accurate, since the gramme is the weight of 1 c.c. of water *at 4° C.* The correction, however, is only made in case a very exact expression is desired, and for ordinary purposes it is omitted. In any case the actual weight may be obtained by multiplying the result by 0·99916.

36·5 grammes of HCl. occupy 22·32 litres;

$$2{\cdot}3352 \text{ grammes occupy } \frac{22{\cdot}32 \times 2{\cdot}3352}{36{\cdot}5} \text{ litres:}$$

$$= 1{\cdot}428 \text{ litres.}$$

The relation between weight and volume of solids, like that of liquids, is expressed in terms of water as unit. Thus, diamond is 3·5 times as heavy as water, and its sp. gr. is 3·5, the sp. gr. of graphite is 2·2, of mercury 13·6.

The weight of these bodies that occupy the same volume as 1 gramme of water (that is, 1 c.c.) is 3·5, 2·2, and 13·6 respectively. This relation is seldom necessary in chemical calculations.

IV.—Calculation of the percentage composition of a body.

When the chemical composition of a body is expressed by symbols, the proportions of the respective elements contained in it are the weights of the elements as determined from the table of atomic weights.

HCl indicates a compound formed by the union of 1 part by weight of hydrogen with 35·5 parts by weight of chlorine.

H_2O indicates a compound formed by the union of 2 parts by weight of hydrogen with 16 parts by weight of oxygen.

CO_2 indicates a compound formed by the union of 12 parts by weight of carbon with 32 (*i.e.* 2 × 16) parts by weight of oxygen.

P_2O_5 indicates a compound formed by the union of 62 (*i.e.* 2 × 31) parts by weight of phosphorus with 80 (*i.e.* 5 × 16) parts by weight of oxygen.

H_3PO_4 indicates a compound formed by the union of 3 parts by weight of hydrogen, 31 parts by weight of phosphorus, and 64 (*i.e.* 4 × 16) parts by weight of oxygen.

36·5	parts by	weight of	HCl	contain	1	pt. of	H and 35·5	pts. of	Cl.
18	,,	,,	H_2O	,,	2	,,	H and 16	,, ,,	O.
44	,,	,,	CO_2	,,	12	,,	C and 32	,, ,,	O.
142	,,	,,	P_2O_5	,,	62	,,	P and 80	,, ,,	O.
98	,,	,,	H_3PO_4	,,	3	,,	H, 31 of P and 64 of O.		

The *percentage* composition is merely the statement of the relative weights of each of the constituents in 100 *parts* of the compound.

Thus, if 18 parts by weight of water contain 2 parts of hydrogen and 16 parts of oxygen, then 100 parts of water will contain—

$$\frac{2 \times 100}{18} \text{ parts of H, } i.e. \ 11{\cdot}11;$$

$$\text{and } \frac{16 \times 100}{18} \quad \text{,, ,, O, } i.e. \ 88{\cdot}88;$$

and this represents the percentage composition of water.

(11) Find the percentage composition of potassium chlorate, $KClO_3$—

$$\begin{aligned} K &= \ 39{\cdot}1 \\ Cl &= \ 35{\cdot}5 \\ O_3 &= \ \underline{48{\cdot}0} \\ & \quad 122{\cdot}6 \end{aligned}$$

$$\text{Percentage amount of K} \quad \frac{39{\cdot}1 \times 100}{122{\cdot}6} = 31{\cdot}89$$

$$\text{,, \quad ,, \quad Cl} = \frac{35{\cdot}5 \times 100}{122{\cdot}6} = 28{\cdot}95$$

$$\text{,, \quad ,, \quad O} = \frac{48 \times 100}{122{\cdot}6} = \underline{39{\cdot}16}$$

$$\underline{\underline{100{\cdot}00}}$$

(12) Find the percentage amount of water of crystallization in $FeSO_4.7\,H_2O$.

$$\begin{aligned} Fe &= \ 56 \\ S &= \ 32 \\ O_4 &= \ 64 \\ 7\,H_2O &= \ \underline{126} \\ & \quad 278 \end{aligned}$$

278 parts of $FeSO_4.7\,H_2O$ contain 126 parts of water.

$$\text{Percentage of water} = \frac{126 \times 100}{278} = 45{\cdot}32.$$

The question which even more frequently arises in practice is the converse one, the determination of the formula of a substance from the results of analysis of the substance. We have seen already that the relative composition by weight of a body is obtained by taking the atomic weight of each constituent, and where more than one atom of any constituent is present, then the multiple of that according to the number of atoms.

E.g., for $COCl_2$—

	Atomic weight.	No. of atoms.	Product.	Percentage composition.
C	12	1	12	12·12
O	16	1	16	16·16
Cl_2	35·5	2	71	71·72

We now reverse the process, and desire to determine the relative number of atoms of each element, having given the composition by weight of a body as deduced from its analysis—

S = 23·7 per cent.
O = 23·7 „ „
Cl = 52·6 „ „

Let n, n', n'' be the number of atoms of S, O, and Cl respectively, the atomic weights being 32, 16, and 35·5, we have the relative weights of each of the constituents—

$$32\,n,\ 16\,n',\ \text{and}\ 35{\cdot}5\,n''.$$

These values are proportional to the weights as represented by the percentage composition, viz.—

23·7, 23·7, 52·6.

Thus—

$32\,n \propto 23{\cdot}7$ and n is proportional to 0·74.
$16\,n' \propto 23{\cdot}7$ „ n' „ „ 1·48.
$35{\cdot}5\,n'' \propto 52{\cdot}6$ „ n'' „ „ 1·48.

The *simplest proportion in whole numbers* is—

1 : 2 : 2,

and the formula on this assumption is—

$$SO_2Cl_2.$$

This, then, is the *empirical formula* as deduced solely from the consideration of the results of the analysis. It is quite consistent with such a calculation that the formula should be $S_2O_4Cl_4$, or $S_3O_6Cl_6$, or any such multiple. Which of these is to be finally accepted can only be decided after a determination of the vapour density of the body, or of its chemical constitution and character, and this would be the *constitutional formula* of the body.

To determine the empirical formula of a body, we therefore divide the results of analysis by the respective atomic weights, and the numbers so obtained are *proportional* to the number of atoms.

(13) The percentage composition of a compound is found to be H = 5·88 and O = 94·12: find its formula.

In this case n and n_1 being in proportion to the number of atoms of hydrogen and oxygen respectively

$n\mathrm{H} = 5{\cdot}88$, and H being 1, $n = 5{\cdot}88$.

$n_1\mathrm{O} = 94{\cdot}12$, and O being 16, $n_1 = 5{\cdot}88$.

The body therefore consists of an equal number of atoms of H and O, and the simplest formula would be HO. Chemical considerations, however, compel us to accept a multiple of this, viz. H_2O_2, as the formula of hydrogen peroxide, the substance whose composition had been ascertained.

(14) Find the formula of a substance having the composition—

Mg = 9·76.
S = 13·01.
O = 26·01.
Water of crystallization = 51·22.

Mg gives $\frac{9{\cdot}76}{24} = 0{\cdot}406$ as proportional number.
S ,, $\frac{13{\cdot}01}{32} = 0{\cdot}406$,, ,,
O ,, $\frac{26{\cdot}01}{16} = 1{\cdot}626$,, ,,
H_2O ,, $\frac{51{\cdot}22}{18} = 2{\cdot}846$,, ,,

From these numbers we deduce as the simplest whole numbers bearing the same relation to one another 1 : 1 : 4 : 7, and the simplest formula for the body is—

$$MgSO_4.7\,H_2O.$$

V.—Application to chemical problems.

We have now considered the fundamental calculations which enter into chemical problems, and a few examples will be given to show how these bear upon questions involving chemical decomposition and interchange.

(15) What weight of caustic soda (NaOH) will be needed to just neutralize 10 c.c. of dilute sulphuric acid (sp. gr. 1·155) containing 21 per cent. of H_2SO_4?

In all cases where a chemical reaction is concerned, involving considerations of weight or volume, it is well to state the reaction in the form of an equation at the outset—

$$2\,NaOH + H_2SO_4 = \underset{\text{Sodium Sulphate.}}{Na_2SO_4} + 2\,H_2O.$$

From this we see that 2 NaOH neutralize H_2SO_4, the respective weight relations being—

$$2\,(23 + 16 + 1) \text{ and } (2 + 32 + 64) \text{ or } 80 : 98.$$

80 parts by weight of caustic soda serve to neutralize 98 parts by weight of sulphuric acid.

Now determine the actual weight of sulphuric acid that is to be neutralized—

10 c.c. of the dilute sulphuric acid (sp. gr. 1·155) weigh 11·55 grms.

21 per cent. of this is H_2SO_4, *i. e.* $\frac{11{\cdot}55 \times 21}{100} = 2{\cdot}4255$ grammes.

Required amount of caustic soda is—

$$\frac{2{\cdot}4255 \times 80}{98} \text{ grammes, or } 1{\cdot}98 \text{ grammes.}$$

(16) What volume of oxygen collected at standard temperature and pressure (0° and 760 m.m.) is given off on heating 10 grammes of mercuric oxide?

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

First determine the *weight* of oxygen from the above equation, which shows that 432 parts of mercuric oxide yield 32 parts of oxygen, or, in simpler numbers, 27 parts yield 2 parts of oxygen.

$$10 \text{ grammes therefore yield } \frac{2 \times 10}{27}, \text{ or } 0{\cdot}74 \text{ grammes.}$$

Now 32 grammes of oxygen occupy at standard temperature and pressure 22·24 litres, and the *volume* of oxygen corresponding to this weight is—

$$\frac{0{\cdot}74 \times 22{\cdot}24}{32} = 514 \text{ cubic centimetres.}$$

(17) What weight of sulphur must be burnt so as to yield 1 litre of sulphur dioxide at standard temperature and pressure?

$$S + O_2 = SO_2.$$

Here we start from a known *volume* of gas and must work back to the *weight* in terms of which the result is to be expressed.

22·24 litres of SO_2 weigh 64 grammes.

1 litre of SO_2 weighs $\frac{64}{22 \cdot 24}$ or 2·867 grammes.

Also 64 grammes of SO_2 contain 32 grammes of S,
and 2·877 „ SO_2 „ 1·4385 „ S.

1·4385 gramme of sulphur will therefore be required to produce 1 litre of SO_2.

Such a calculation may, however, be shortened by the consideration that as 32 grammes of sulphur, according to the equation, yield 64 grammes or 22·24 litres of SO_2,

$\frac{32}{22 \cdot 24}$ grammes will yield 1 litre of SO_2.

The next example will be rendered more complex by introducing conditions of temperature and pressure differing from the standard. No further difficulty is really involved, except that the correction for temperature and pressure must be made.

(18) 2½ litres of nitrous oxide have been collected at 39° C. and 741 m.m. pressure; what weight of ammonium nitrate has been decomposed in order to supply the gas?

First eliminate the irregularity introduced by the temperature and pressure, by determining what volume the gas would have occupied had it been collected at standard temperature and pressure. This will be—

$$\frac{2\ 5 \times 273 \times 741}{312 \times 760} \text{ litres, or } 2 \cdot 133 \text{ litres.}$$

Now according to the equation—

$$\underset{\text{Ammonium Nitrate.}}{NH_4NO_3} = \underset{\text{Nitrous Oxide.}}{N_2O} + 2\,H_2O.$$

80 grammes of ammonium nitrate yield 44 grammes (or 22·24 litres) of nitrous oxide, and hence

$\frac{80 \times 2 \cdot 133}{22 \cdot 24}$ grammes, or 7·673 grammes, of ammonium nitrate have been decomposed.

(19) One gramme of water is (*a*) converted into steam at 100° C., (*b*) decomposed by means of sodium and the hydrogen collected at 13° C.; what volume will each occupy, the barometer at the time standing at 750 m.m.?

First, let us consider the case of the steam. This being water vapour has, at standard temperature and pressure, a density such that, as previously shown,

18 grammes is the weight of 22·24 litres.

$$\text{Thus 1 gramme occupies } \frac{22{\cdot}24}{18} \text{ or } 1{\cdot}235 \text{ litres.}$$

At 100° C. and 750 m.m. pressure this occupies—

$$\frac{1{\cdot}235 \times 373 \times 760}{273 \times 750} = 1{\cdot}71 \text{ litres.}$$

Secondly, as to the hydrogen, the decomposition is represented by the equation—

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2\,;$$

from which we see that 36 grammes of water yield 2 grammes of hydrogen, and therefore 1 gramme of water yields $\frac{1}{18}$ gramme of hydrogen.

The *volume* of hydrogen at standard temperature and pressure is thus $\frac{11{\cdot}12}{18}$ or 0·62 litre. Corrected so as to represent the volume at 13° C. and 750 m.m. pressure this becomes—

$$\frac{0{\cdot}62 \times 286 \times 760}{273 \times 750} = 0{\cdot}658 \text{ litre.}$$

The whole of the more important elements entering into the treatment of chemical problems have now been discussed, and it only remains to add some examples in further illustration of their application to chemical reactions.

(20) 10 grammes of mercury are heated with excess of concentrated sulphuric acid and the sulphur dioxide formed is collected at 15° C. and 765 m.m. pressure; what volume does it occupy?

Here, as in most cases, it is best to commence by a statement of the reaction which takes place.

$$Hg \quad + \quad 2\,H_2SO_4 \quad = \quad \underset{\text{Mercuric Sulphate.}}{HgSO_4} \quad + \quad 2\,H_2O \quad + \quad SO_2.$$

200 grammes of mercury give 64 grammes of SO_2,
or 200 „ „ „ 22·24 litres of SO_2.
10 „ „ „ 1·112 „ „

at standard temperature and pressure.

Volume at 15° C. and 765 m.m. pressure is then

$$\frac{1{\cdot}112 \times 288 \times 760}{273 \times 765} = 1{\cdot}165 \text{ litre.}$$

(21) 25 c.c. of marsh gas (CH_4) are mixed with 500 c.c. of air and exploded in a eudiometer; what volume of gas should there be (*a*) before the removal of the carbon dioxide formed, (*b*) after the absorption of the carbon dioxide by means of caustic potash? The temperature and pressure may be assumed to be the same when each of the readings of volume were taken.

The chemical reaction which takes place is

$$\underset{2\text{ vols.}}{CH_4} + \underset{4\text{ vols.}}{2\ O_2} = \underset{2\text{ vols.}}{CO_2} + 2\ H_2O,$$

the nitrogen of the air taking no part in the combustion.

It is further manifest on inspection that the 2 volumes of marsh gas and 4 volumes of oxygen, before explosion, give rise to 2 volumes of carbon dioxide, the space occupied by the water being negligible.

Thus 6 volumes are reduced to 2, and the diminution is 4 volumes.

But the marsh gas occupies 25 c.c., and is represented by 2 volumes.

The diminution in volume is therefore 50 c.c., and the 525 c.c. of mixed gases originally present in the eudiometer have been reduced to 475 c.c.

Similarly the CO_2 occupies the same volume as the marsh gas from which it was obtained, and is thus 25 c.c., and if this be removed there will remain 450 c.c. of gas in the eudiometer. The result is that the residual gas—

(*a*) before removal of CO_2 is 475 c.c.
(*b*) after „ „ „ 450 c.c.

(22) 10 c.c. of liquid carbon bisulphide (sp. gr. 2·63) are burnt in oxygen; find the volume of the resulting gases measured at standard temperature and pressure.

We must first ascertain the weight of the carbon bisulphide. Its sp. gr. being 2·63, the 10 c.c. will weigh 26·3 grammes.

The chemical change during combustion is represented in the equation

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

76 grammes of CS_2 yield 44 grammes or 22·24 litres CO_2.
„ „ „ „ 128 „ „ 44·48 „ SO_2.
„ „ „ „ 66·72 litres of CO_2 and SO_2 together.

26·3 grammes of CS_2 yield $\frac{66·72 \times 26·3}{76} = 23·09$ litres.

(23) Considering air as a mixture of 79 per cent. by volume of nitrogen with 21 per cent. by volume of oxygen, find the density of air compared with hydrogen. Also find the density of the vapour of carbon bisulphide compared with air.

79 vols. of nitrogen	are as heavy as	79 × 14, or	1,106	vols.	of H.
21 ,, oxygen	,, ,,	21 × 16, or	336	,,	,,
100 ,, air	,, ,,		1,442	,,	,,

Density of air is 14·42.[1]

Density of the vapour of bisulphide of carbon is $\frac{12 + 64}{2}$ or 38, compared with H.

Compared with air it is therefore $\frac{38}{14·42} = 2·635$.

Atomic weights to be used in the following calculations.

Hydrogen,	1.	Chlorine,	35·5.
Carbon,	12.	Potassium,	39.
Nitrogen,	14.	Calcium,	40.
Oxygen,	16.	Iron,	56.
Sodium,	23.	Bromine,	80.
Magnesium,	24.	Silver,	107·6.
Phosphorus,	31.	Antimony,	119·6.
Sulphur,	32.	Mercury,	200.
Lead,	206·4.		

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[1] Actual density at normal composition is taken as 14·435.

CHEMICAL PROBLEMS.

1. The volume of a permanent gas at 0° C. is 3 litres; at what temperature would it occupy 4 litres, the pressure remaining unaltered?
2. Two samples of gas occupy the same volume, but one is at − 20° C., and the other at 20° C.; what is their relative volume when both are at 0° C.?
3. The volume of a gas at 13° C. is 100 c.c.; find its volume at − 130° C., at − 13° C., and at 130° C.
4. A gas under standard atmospheric pressure measures 209 c.c.; what volume will it occupy under a pressure of $\frac{1}{10}$, $\frac{1}{2}$, 2, and $5\frac{1}{2}$ atmospheres respectively?
5. What volume will half a litre of gas measured at 750 m.m. pressure occupy when subjected to a pressure of 850 m.m. of mercury?
6. A rectangular vessel 10 c.m. long, 5 c.m. wide, and 3·5 c.m. deep, is filled with gas at 100° C. and 770 m.m. pressure; what volume will the gas occupy at standard temperature and pressure?
7. A sample of gas is collected in a eudiometer, and it is found that the level of the mercury in the eudiometer is 257 m.m. above that of the trough, also the height of the barometer at the time is 745 m.m.; under what pressure is the gas?
8. A sample of gas is collected at standard temperature and pressure, and the pressure is then doubled, and the temperature gradually raised until the volume of the gas is the same as it was originally; at what temperature does this occur?

9. Under how many atmospheres pressure will steam have the same density as water (1 c.c. weighs one gramme), if the contraction takes place in accordance with Boyle's law, and the temperature remains at 600° C. ?

10. If the temperature remains at zero, at what pressure will hydrogen have a density equal to 0·62 of that of water, this being the density found by Dewar for hydrogenium ?

11. One cubic centimetre of bromine (density 3·2) is transformed into vapour at 78° C. ; determine the volume occupied by the vapour.

12. The sp. gr. of pure nitric acid being 1·522, find the weight of 100 c.c. of it, and the volume that you must take to weigh 100 grammes.

13. What volume of such acid will be required to just neutralize 100 grammes of caustic potash (KOH), and what weight of potassium nitrate is formed ?

14. Calculate the percentage composition of calcium carbonate ; what percentage of carbon dioxide does it contain ?

15. Chlorine forms with water a solid hydrate, having the composition $\mathrm{Cl_2.\ 10\ H_2O}$; calculate the percentage of hydrogen, chlorine, and oxygen contained in this body.

16. Find the empirical formula of a compound consisting of 46·66 per cent. of iron and 53·33 per cent. of sulphur.

17. An oxide of iron contains 72·3 per cent. of iron ; determine its empirical formula.

18. Determine the simplest formula for a salt having the following percentage composition—

Sodium,	29·36.
Phosphorus,	26·38.
Oxygen,	44·26.
	100·00.

19. A solution of caustic soda having the sp. gr. 1·32 contains 28·8 per cent. of NaOH ; what weight of sulphuric acid is required to be just sufficient to neutralize a litre of such a solution ?

20. What volume of sulphuretted hydrogen at 13° C. and 798 m.m. pressure is required to effect the complete precipitation of one gramme of corrosive sublimate, $\mathrm{HgCl_2}$?

21. What weight of pure antimony sulphide, Sb_2S_3, should yield a litre of sulphuretted hydrogen collected at 10° C. and 760 m.m. pressure?

22. Determine the volume of chlorine required to convert 10 grammes of phosphorus into the pentachloride.

23. A gramme of common salt is dissolved in water and excess of silver nitrate solution is added; what weight of silver chloride should be precipitated?

24. Calculate (*a*) the volume, (*b*) the weight, of carbon dioxide in the air of a room 6 mètres long, 4 mètres wide, and 3 mètres high, if there is 1 volume of this gas present per 1,000 volumes of the air.

25. Dumas determined the relative amounts of nitrogen and oxygen in air by passing it over heated copper. He found—

Weight of tube and copper before experiment,	120 grms.
,, ,, ,, ,, ,, after ,,	121·15 ,,
,, ,, globe when exhausted	852 ,,
,, ,, ,, and nitrogen	855·85 ,,

From these numbers calculate the percentage composition of air by weight, and deduce its percentage composition by volume.

26. Dumas determined the composition of water synthetically by passing hydrogen over heated copper oxide, and found—

Weight of tube and copper oxide before experiment,	334·598 grs.
,, ,, ,, ,, ,, ,, after ,,	314·236 ,,
,, ,, drying tubes before experiment ...	426·358 ,,
,, ,, ,, ,, after ,, ...	449·263 ,,

Calculate the percentage composition of water by weight.

27. Ten grammes of steam are passed over red-hot iron; what volume of hydrogen at 26° C. and 741 m.m. pressure will be obtained if one-third of the steam undergoes decomposition?

28. Fifteen cubic centimetres of ammonia are completely decomposed by electric sparks, and then 40 c.c. of oxygen are added and the mixed gases exploded; state the gases present and the volume of each (*a*) just before exploding, (*b*) after exploding.

29. A mixture of 10 litres of oxygen with one litre of carbon dioxide is shaken up with 100 c.c. of water; determine the volume of each gas that will be dissolved—the barometer at the time standing at 760 m.m. and the thermometer at zero.

30. Make the same determination with a mixture of one litre of oxygen and 10 litres of carbon dioxide.

31. A litre of sea-water (sp. gr. 1·03) is evaporated to dryness, and found to leave as residue 36·4 grammes of salts; find the percentage of solid matter in the sea-water.

32. Given that a mètre is equivalent to 39·37 inches, calculate the number of cubic inches in a litre, and the number of litres in a cubic foot.

33. Determine the percentage of carbon in cane-sugar ($C_{12}H_{22}O_{11}$) and the volume of carbon dioxide that results from the combustion of 0·2 gramme of sugar.

34. A mixture of 20 c.c. of ethylene and 200 c.c. of oxygen is exploded in a eudiometer; what volume of gas remains after the explosion, and what volume when the carbon dioxide is subsequently removed by absorption with potash?

35. What quantity of crystallized oxalic acid ($C_2H_2O_4 . 2\ H_2O$), heated with excess of sulphuric acid, will yield 5 litres of gas at standard temperature and pressure?

36. If 50 c.c. of sulphuretted hydrogen be mixed with excess of chlorine, what volume of hydrochloric acid will be formed, and what weight of sulphur liberated?

37. A gramme of a substance containing carbon is heated with lead oxide, and found to form 10 grammes of metallic lead; what percentage of carbon was present?

38. What weight of iron must be dissolved in dilute sulphuric acid in order to yield sufficient hydrogen to fill a balloon having a capacity of 100 cubic mètres?

39. Ten grammes of carbon are burnt in 1,000 litres of air (taken as consisting of 79 vols. of N and 21 of O) at 15° C. and 700 m.m. pressure; find the percentage of nitrogen, oxygen, and carbon dioxide in the air after the combustion is complete.

ANSWERS TO CHEMICAL PROBLEMS.

1. 91°.
2. 293 : 253.
3. 50 c.c., 90·9 c.c., 140·9 c.c.
4. 2090 c.c., 418 c.c., 104·5 c.c., 38 c.c.
5. 441 c.c.
6. 129·7 c.c.
7. 488 m.m.
8. 273° C.
9. 3,951 atmospheres.
10. 6,894 atmospheres.
11. 571·9 c.c.
12. 152·2 grammes ; 65·7 c.c.
13. 73·9 c.c. ; 180·4 grammes.
14. Ca = 40 per cent.
C = 12 ,,
O = 48 ,,
44 per cent.
15. H = 7·97 per cent.
Cl = 28·28 ,,
O = 63·75 ,,
16. FeS_2.
17. Fe_3O_4.
18. $Na_6P_4O_{13}$.
19. 465·7 grammes.
20. 81·9 c.c.
21. 4·847 grammes.
22. 17·93 litres.
23. 2·446 grammes.
24. 72 litres ; 142·4 grammes.
25. Oxygen, 23 ; Oxygen, 20·7.
Nitrogen, 77; Nitrogen, 79·3.
26. Hydrogen, 11·1.
Oxygen, 88·9.
27. 4·626 litres.
28. (*a*) N = 7·5 c.c.
H = 22·5 c.c.
O = 40·0 c.c.
(*b*) N = 7·5 c.c.
O = 28·75 c.c.
29. Oxygen = 3·73 c.c.
Carbon dioxide = 16·36 c.c.
30. Oxygen = 0·37 c.c.
Carbon dioxide = 163·6 c.c.
31. 3·534 per cent.
32. 61023 ; 28·317.
33. 42·1 per cent.
·157 litre.
34. 180 c.c. ; 140 c.c.
35. 14·16 grammes.
36. 100 c.c. ; 0·0719 gramme.
37. 29 per cent.
38. 251·8 kilogrammes.
39. Nitrogen, 79.00 per cent.
Oxygen, 19·2 ,, ,,
Carbon dioxide, 1·8 ,, ,,

APPENDIX IV.

EXPERIMENTS

THE chemistry of the metals and their compounds opens up a very wide field, and the presentment frequently given is little more than a systematized record of the preparation and chief properties of these bodies.

It is certainly essential that the process of investigation so generally insisted on in the case of the non-metals should be continued with the metals, though there seem to be few schools where this is fully recognized.

In the following pages I have given a list of experiments which, whilst it lays no claim to being exhaustive or even complete, will I hope suggest the lines along which work in the laboratory might with advantage be undertaken.

Furthermore, since at this stage the student ought to have acquired some proficiency in planning and executing experiments, I have not thought it necessary to do more than indicate in general terms the problem to be investigated, leaving the rest to be filled in by reference to the text and by the exercise of such ingenuity and skill as may fairly be expected of one who has followed with diligence the course prescribed in the previous volume of this work.

CHAPTER I.

1. Compare the weights of equal volumes of hydrogen and air.

2. Devise an experiment to show that if the pressure on a gas is doubled, the volume occupied by the gas is halved.

3. Show by experiment (1) that CO_2 is heavier than air, and (2) that yet if CO_2 be introduced into the lower part of a tall cylinder of air, some of the heavier gas will soon be found in the upper part of the cylinder.

4. Determine the vapour density of carbon tetrachloride by the method of Dumas.

5. Determine the vapour density of iodine or stannic chloride by the method of Victor Meyer.

6. Drop a fragment of ammonium chloride into a red hot crucible and test the fumes which come off with a moistened litmus paper.

7. Fill a small two-ounce bottle with nitrogen peroxide, stopper it tightly, and then leave it in boiling water, and note the change of colour of the gas.

8. Show by experiment that CO_2 contains its own volume of oxygen.

9. Fill a small two ounce bottle over water about two-thirds with hydrogen and the rest with chlorine in diffused daylight, stopper it carefully, and leave it in this light a day or so. Note (*a*) that colour of chlorine has gone, (*b*) that when the stopper is removed over mercury no alteration in volume has occurred, (*c*) that when the bottle is brought over a solution of potassium iodide much of it is absorbed but no iodine is liberated, (*d*) that the residual gas is hydrogen.

10. Introduce equal volumes of CO and oxygen into a eudiometer over the mercury. Explode, allow to cool, and note the decrease of volume and also the effect of introducing a piece of caustic soda into the gas. Equal volumes of the gases may be obtained by using a small specimen tube as the measure.

CHAPTER II.

1. Expose a 50 gramme brass weight to boiling water or steam for some minutes, and then *immediately* bring it into 100 c.c. of water in a small beaker. The temperature of the water (which should be that of the room) is to be taken before the weight is put in, and after it has been stirred in contact with the weight for a minute.

2. Place a strip of zinc and one of platinum in dilute sulphuric acid, attach platinum wires to the strips and insert the free ends of the wires in the two limbs of a U-tube containing a solution of sodium sulphate tinted with litmus.

3. Repeat this experiment, using a solution of lead nitrate instead of sodium sulphate.

4. Pass the current from two Grove's or Bunsen's cells through a voltameter containing acidulated water and (connected up in the same circuit) a solution of lead nitrate. When 100 c.c. of hydrogen have collected, disconnect the wires and rapidly pour off the liquid from the lead which has separated. Wash it by decantation, dry and weigh, and compare its weight with that of the hydrogen as calculated from its volume. Deduce the electrochemical equivalent of lead.

5. Measure the amount of hydrogen evolved when a known weight (about half a gramme) of zinc is dissolved in excess of dilute sulphuric acid and deduce the equivalent of zinc.

6. Do the same experiment with aluminium and warm caustic soda solution, and deduce the equivalent of aluminium.

CHAPTER III.

1. Introduce a known weight (about 100 grms.) of snow or freshly broken ice into a breaker. Pour on it 5 times its weight of warm water at a known temperature (about 30°C). Stir well till the ice is all melted and take the temperature. Deduce the latent heat of fusion of ice.

2. Pass steam into 200 c.c. of water at the temperature of the room until an increase of 30°C is noted. Weigh the beaker and thus ascertain how much steam has been condensed. Deduce the latent heat of steam.

3. Determine the depression of temperature which takes place when 100 grms. of powdered ammonium nitrate is well stirred with the same weight of water.

4. Make a saturated solution of common salt in water at the temperature of the room, and evaporate to dryness on a water bath so as to find the solubility of the salt in water.

5. Devise a method for determining the solubility of carbon dioxide in water.

6. Evaporate 100 c.c. of sea water to dryness and weigh the amount of residue.

7. Make a soap solution by dissolving about half a gramme of soap shavings in 100 c.c. of weak alcohol. Add this solution a few drops at a time to each of the following till on shaking in a stoppered bottle a lather is obtained which lasts 3 minutes: (*a*) 50 c.c. of distilled water, (*b*) 50 c.c. of the ordinary tap water, (*c*) 50 c.c. of distilled water to which 1 c.c. of lime water has been added.

8. Mix oxygen with six times its volume of hydrogen and introduce some of the mixture into a eudiometer. Read off the height of the mercury, pass the spark and again read the height of the mercury after cooling. Determine the diminution in volume of the gas and the composition of water.

9. Examine what takes place when hydrogen peroxide is added to (*a*) a solution of potassium iodide, (*b*) a solution of potassium permangate.

10. Examine the action of ozone on (*a*) a solution of potassium iodide, (*b*) a solution of litmus, (*c*) a globule of mercury.

11. Ascertain the amount of oxygen in air by the action of phosphorus.

12. Leave some solid calcium chloride and some solution of baryta exposed for a time to air, and note the changes which occur.

CHAPTER IV.

1. Add water little by little to sulphuric acid until acid of the specific gravity 1·7 is obtained; heat 4 parts by weight of this with 5 parts of sodium nitrate into a retort and condense the nitric acid which comes over.

2. Prepare hydrochloric acid by *gently* heating 200 grms. of common salt with sulphuric acid; pass the gas into 200 c.c. of water in a half litre flask kept cool, and when fully saturated

measure the volume of the liquid and determine its specific gravity. By consulting tables ascertain the percentage of HCl in the liquid.

3. See what takes place (*a*) when a current of air is passed through the liquid obtained above, (*b*) when some of the liquid is boiled in an open vessel, (*c*) when it is diluted with twice its volume of water and then boiled.

4. Heat a few fragments of iron pyrites in an inclined tube open at both ends, and note the nature of the products which pass up the tube and of the residue left.

5. Pass nitric oxide into a litre bottle till dark brown fumes are manifest ; now pour in 200 c.c. of concentrated sulphuric acid and stopper, shake up and observe the absorption of the fumes. Finally add an equal volume of dilute sulphuric acid and the fumes reappear.

6. Pour 100 c.c. of commercial oil of vitrol into a litre of water and allow to stand ; a white turbidity indicates the presence of lead. Allow to settle and then pass H_2S through some of the clear liquid to precipitate any arsenic which may be present.

CHAPTER V.

1. Pass chlorine into ice cold water until the solid hydrate separates.

2. Fill a test-tube with water saturated with chlorine, invert it over water, and expose to bright sunlight ; observe the bubbles of gas given off, and ascertain what the gas is.

3. Gently heat manganese dioxide in a current of hydrochloric acid gas.

4. Mix concentrated sulphuric acid with powdered fluorspar to a paste in a leaden dish ; place in a draught cupboard and cover with a watch glass so that the glass may be etched.

5. Examine the action of strong sulphuric acid on calcium chloride.

6. Prepare hydriodic acid gas ; pass some of the gas through a glass tube heated with a Bunsen burner and see what takes place. Make a solution of hydriodic acid gas in water.

7. Suspend iodine in water and pass a rapid stream of sulphuretted through the liquid.

8. Dissolve 5 grammes of barium chlorate in water and add 1 cc. of concentrated sulphuric acid. What is the nature of the clear solution which is obtained when settling ?

9. Prepare a sample of potassium bromate.

10. Starting from potassium chlorate prepare a specimen of the perchlorate.

11. Examine the action of concentrated nitric acid on iodine.

CHAPTER VI.

1. Prepare a specimen of amorphous phosphorus.

2. Starting from ordinary phosphorus prepare phosphorus pentoxide and examine the action of water on this oxide.

3. Prepare orthophosphoric acid by acting upon phosphorus with nitric acid. Using the product make normal sodium phosphate.

4. Prepare some hypophosphorous acid and examine its action on nitrate of silver and sulphate of copper.

5. Examine the action of chlorine and iodine on phosphorus.

6. Repeat the characteristic tests for metaphosphates, orthophosphates and pyrophosphates using aqueous solutions of the alkali salts.

7. Examine the action of water on phosphorus trichloride and pentachloride respectively.

CHAPTER VII.

1. Make an intimate mixture of fine sand or kaoline with six times its weight of potassium carbonate and heat to redness for an hour. Extract with water and prepare gelatinous silica.

2. Prepare silicon tetrafluoride and using this obtain (*a*) gelatinous silica (*b*) a solution of hydrofluosilicic acid.

3. Starting with a solution of an alkaline silicate prepare an aqueous solution of silica.

4. Starting from borax prepare boric acid and boron trioxide.

5. Prepare boron hydride.

CHAPTER VIII.—

1. Cut a piece of sodium (fingers and knife to be quite dry) and note silvery lustre, also rapid tarnishing.

2. Heat a piece of sodium or potassium (free from oil) the size of a pea in a stream of hydrogen and note the colour of the vapour.

3. Drop similar pieces of these metals into about 100 c.c. of water and note what takes place. Stand a little away while the action is proceeding. Test the water afterwards with red and blue litmus paper.

4. Leave similar pieces of the metals exposed to the air for a day and notice the change they undergo. Treat them subsequently as in (3).

5. Heat similar pieces in air in iron boats for 15 minutes, allow to cool, and then drop the boats into a solution of potassium iodide. Proof will be obtained of the formation of *peroxide.*

6. Neutralize dilute hydrochloric acid with caustic soda and prepare good crystals of common salt. Sketch them.

7. Prepare a sample of potassium iodide and (starting from milk of lime) one of potassium chlorate.

8. Convert NaCl into Na_2SO_4.

9. Convert $NaHCO_3$ into Na_2CO_3 and soda crystals into $NaHCO_3$.

10. Heat strongly for an hour or so, an intimate mixture of fine white sand or silica with five times its weight of sodium carbonate ; note the effervescence of CO_2. Allow to cool and then add HCl till strongly acid, boil to complete dryness on a water bath, extract with water, and silica is left as a residue, sodium chloride passing into solution. Formulate the chemical changes concerned.

CHAPTER IX.—

1. Heat about a gramme (carefully weighed) of powdered calcite or calcium carbonate over the blowpipe flame and ascertain the weight of the residue when it is found that no further loss of weight occurs. A rough estimation of the combining weight of calcium may thus be made.

2. Pour about 100 c.c. of water on a lump of quick-lime, and note the heat developed and the formation of the hydroxide.

3. Heat baryta until on throwing some of the product into a solution of KI and HCl a marked liberation of iodine occurs. See if the original baryta gives any liberation of iodine.

4. Reduce $CaSO_4$ to the sulphide (*a*) by heating an intimate mixture of the sulphate with coal, (*b*) by heating a fragment on platinum wire in the reducing flame of a Bunsen burner. Note H_2S evolved when the product is acidified.

5. Shake up $CaSO_4$ with much water; allow to settle, and add some of the clear solution to solutions of (*a*) strontium chloride, (*b*) barium chloride, (*c*) ammonium carbonate, (*d*) ammonium oxalate.

6. Examine the changes which take place when bleaching powder is warmed with solutions of potassium iodide and cobalt nitrate respectively, and also when CO_2 is passed through bleaching powder well stirred up with water.

7. To a concentrated solution of barium chloride add an equal volume of concentrated hydrochloric acid.

8. Examine the action of calcium carbide on water.

9. Prepare barium nitrate in crystals, starting with heavy spar.

CHAPTER X.—

1. Convert magnesite into magnesia, and then from this prepare crystallized magnesium chloride.

2. Heat the magnesium chloride, raising the temperature gradually, and examine the products given off.

3. Prepare magnesium nitride and see how it reacts with water and with dilute hydrochloric acid.

4. Prepare and sketch crystals of $Mg(NH_4)PO_4.6H_2O$.

5. Weigh about a gramme of zinc, transform it into oxide by treatment with concentrated nitric acid in a porcelain crucible; weigh the oxide and determine the atomic weight of zinc (oxygen = 15·88).

6. Starting from zinc blende, prepare crystals of zinc sulphate.

7. Make sodium amalgam and examine its action upon water.

8. Dissolve a globule of mercury (*a*) in dilute nitric acid, (*b*) in concentrated nitric acid; add dilute hydrochloric acid to each of

the liquids so obtained. What inferences do you draw from these experiments?

9. Convert HgCl into $HgCl_2$, and $HgCl_2$ into HgCl.

10. Prepare Nessler's reagent, and examine its action on water containing very small quantities of ammonia.

11. Obtain metallic mercury from cinnabar.

CHAPTER XI.—

1. Prepare a solution of sodium aluminate by digesting powdered bauxite with a concentrated solution of caustic soda. Pass a current of CO_2 through the liquid so obtained.

2. Examine the action of the following reagents on aluminium foil, (*a*) dilute HCl, (*b*) dilute H_2SO_4, (*c*) solution of caustic soda.

3. Prepare the colloidal form of aluminium hydroxide.

4. Prepare crystals of ammonium alum.

5. Make a saturated solution of the sulphate or acetate of aluminium at the ordinary temperature, decant off some of the clear liquid and boil it for two or three minutes. See if the precipitate which has separated on boiling is readily dissolved by the addition of dilute sulphuric acid.

6. Do an experiment to illustrate the use of aluminium salts in throwing down and fixing organic colouring matters on cotton.

7. Determine the amount of potash alum in 100 c.c. of a saturated solution at the temperature of the room by leaving excess of the powdered salt in contact with say 250 c.c. of water for some hours (with occasional agitation), and then evaporating 100 c.c. of the clear supernatant liquid.

8. Boil ultramarine with dilute hydrochloric acid for some minutes and see if any change is manifest. Ascertain whether the hydrochloric acid has dissolved any of the substance.

CHAPTER XII.—

1. Dissolve about a gramme of copper sulphate in 100 c.c. of water and immerse a steel rod in the solution till the whole of the copper is precipitated. Ascertain what the solution now contains.

2. Given metallic copper, prepare cuprous chloride, cuprous oxide, and cupric sulphate.

3. Prepare crystals of $CuSO_4.(NH_3)_4.H_2O$.

4. To a solution of silver nitrate add HCl; show the solubility of AgCl in ammonia and its reprecipitation with nitric acid, also its solubility in a strong solution of common salt and precipitation therefrom (as AgI) by potassium iodide.

5. Dissolve AgCl in a solution of sodium thiosulphate and investigate the action of dilute HCl on this.

6. Extract silver from an alloy of silver and lead by cupellation.

7. Prepare a solution of pure $PtCl_4$ from the crude solution.

8. Prepare platinum sponge and show its power of absorbing hydrogen.

CHAPTER XIII.—

1. Dissolve in concentrated HCl, fragments (*a*) of white pig iron, and (*b*) grey pig iron, noting differences in the residues obtained and the gas evolved in each case.

2. Starting from metallic iron, prepare a solution of ferric chloride and reduce this to ferrous chloride.

3. Prepare soluble and insoluble prussian blue.

4. Dissolve one gramme of $KMnO_4$ in 250 c.c. of water, and also 10 grammes of ferrous ammonium sulphate in 200 c.c. of water. Take 25 c.c. of the latter solution, add an equal volume of dilute sulphuric acid and determine (using a burette) the volume of the permanganate solution that must be added before a permanent pink colouration remains.

5. Dilute 3 or 4 c.c. of the solution of ferrous ammonium sulphate tenfold and add a few drops of ammonia, note the colour of the precipitate (ferrous hydroxide) obtained and its gradual change to reddish brown (ferric hydroxide) on standing or more rapidly when contact with air is promoted by shaking.

6. Prepare solutions of the sulphates of nickel and cobalt from the respective oxides and examine the action of ammonia upon them.

7. Prepare solutions of (*a*) the double cyanide of nickel and potassium, (*b*) the double cyanide of cobalt and potassium, and examine their behaviour when digested with sodium hypochlorite.

CHAPTER XIV.—

1. Examine the effect of heating in air and in a current of hydrogen chloride (*a*) finely powdered spathic iron ore, (*b*) pyrolusite.

2. Prepare manganese dioxide in the wet way, dry it and from it obtain a sample of MnO; finally convert this into Mn_3O_4.

3. Prepare MnO_3 according to Franke's method.

4. Starting from pyrolusite, prepare a solution of potassium manganate, and then convert this into permanganate.

5. To some of this permanganate add an equal volume of dilute sulphuric acid, and determine the effect of passing a current of H_2S through the solution.

6. Starting from pyrolusite prepare a sample of manganous chloride in a crsytallized condition.

7. Using manganous chloride obtain from it in the moist condition specimens of the hydroxide and the sulphide, and observe the changes which take place when these bodies are respectively heated in air.

8. Prepare crystalline manganous sulphate from the chloride.

CHAPTER XV.—

1. Prepare a sample of Cr_2O_3 in the dry way and one of $Cr_2(OH)_6$ by precipitation; dissolve the latter in dilute hydrochloric acid and then boil down to dryness on a water-bath.

2. Dissolve chrome alum in cold water, boil some of the solution for a few minutes, noting any change in colour. To each of these solutions add sodium phosphate.

3. Starting from potassium chromate, prepare crystals of potassium bichromate.

4. Prepare CrO_3, and using this, obtain a specimen of the liquid CrO_2Cl_2.

5. Show that chromic and hydrochloric acids are formed when water is added to CrO_2Cl_2.

6. Obtain a solution of chromous chloride ($CrCl_2$) and note the effect of shaking it up with air in a test tube.

7. Pass H_2S for some minutes through an acidified solution of potassium bichromate.

CHAPTER XVI.—

1. Obtain metallic tin from tinstone and stannic oxide from metallic tin.

2. Pass H_2S through acid solutions of stannous and stannic chloride respectively, and note the character of the precipitates produced.

3. Digest each of these precipitates (well washed) with ammonium sulphide.

4. Prepare a specimen of stannic chloride, and from this crystals of $(NH_4)_2SnCl_6$.

5. Roast a few fragments of galena in a tube open at both ends and held in an inclined position, and note the nature of the products formed.

6. From minium prepare a sample of (*a*) litharge, (*b*) lead dioxide.

7. Prepare a solution of basic acetate of lead and from this "white lead."

8. From white lead prepare in crystals samples of $PbCl_2$, PbI_2 and $Pb(NO_3)_2$.

CHAPTER XVII.—

1. Roast mispickel in an open inclined tube and identify the products formed.

2. Convert a few grains of metallic arsenic into crystals of arsenic trioxide and examine these with a lens.

3. Starting from arsenic trioxide obtain samples of arsenite and arsenate of silver.

4. Prepare sodium thioarsenate, and from this, arsenic pentasulphide.

5. Apply Marsh's and Reinsch's tests in detecting arsenic in realgar or orpiment.

6. Prepare Sb_2O_3 and Sb_2O_5 from metallic antimony.

7. Prepare $SbCl_3$ and investigate the action of water upon it.

8. Prepare potassium antimonate and sodium pyroantimonate.

9. Given Bi_2O_3, prepare the dioxide and pentoxide.

10. Prepare $Bi(NO_3)_3$ and examine the products formed by the action of water upon it.

APPENDIX V

Examination questions set by the Science and Art Department for the Second or Advanced Stage in Chemistry.

1889.

1. Explain the distinctions between an empirical formula, a rational formula, and a constitutional formula.

2. Of what use is a knowledge of the specific heat of an element to the chemist?

3. How can potassium chloride, hypochloride, and chlorate be obtained by the action of chlorine upon caustic potash? Give the composition and properties of these salts.

4. State what experiments you would make to prove that when two substances, *A* and *B*, separately combine with a third substance, *C*, the proportions of *A* and *B* which unite with *C* are measures or multiples of the proportions in which *A* and *B* combine together.

5. Group the following elements according to their valency (atomicity): bismuth, copper, tin, lead, sodium, arsenic, mercury, iron, potassium, calcium, silicon, silver.

Explain the meaning of the terms atomic and molecular weight.

6. How is iodine prepared, and how may it be converted into hydriodic, iodic, and periodic acids?

7. 300 c.c. of a solution of caustic potash containing 40 grammes KHO per litre is required to neutralise 100 c.c. of sulphuric acid, and the same volume of nitric acid. Calculate the amount of acid in each solution.

8. How are lead, mercury, arsenic, zinc, and antimony obtained from their respective sulphides?

9. Give the chemical formulae of the following substances; galena, rock salt, dolomite, fluorspar, heavy spar, borax, calomel.

10. Give some account of the more important compounds of silicon.

1890.

1. Explain the meaning of the terms atomic weight and molecular weight.

2. What is the "specific heat" of an element? How is it determined, and of what value is it in chemical classification?

3. By what experimental methods has the composition of the oxides of carbon been established?

4. How would you prepare a solution of hydrogen dioxide? What is its action on oxide of silver, baryta solution, and potassium iodide?

5. What is the difference between silicon, silica, and silicic acid? How could you obtain all these substances from felspar?

6. Give some account of the metal aluminium, and the composition, preparation, and properties of alumina, aluminium chloride, aluminium sulphate, and common alum.

7. From what minerals is arsenic obtained? How can the two oxides be prepared from the element? Describe their properties, and the properties of the acids obtained from them.

8. How can you prepare the following bodies, directly or indirectly, from iron pyrites: the allotropic forms of sulphur; sulphur dioxide; sulphurous acid; hydrogen sulphide?

9. Ammonia gas is passed into the following solutions: nitric acid; ferric chloride; ferrous chloride; mercuric chloride; silver nitrate; bleaching powder; copper sulphate; water. What happens in each case?

10. Give a short account of the method of manufacture of sulphuric acid (oil of vitriol).

1891.

$H = 1. \quad S = 32. \quad Cl = 35\cdot5. \quad Fe = 56.$

1. Describe how common salt may be converted into soda-ash, soda-crystals, and caustic soda.

2. What is an acid? Give six examples of acids, and point out the basicity of each, explaining by the use of constitutional or graphic formulae, the differences you recognise.

3. How is bleaching powder made? What is its composition, and what views have been held respecting its constitution? How do you explain its bleaching action?

4. How has the element fluorine been isolated? Give some account of its properties, and describe its combinations with hydrogen and silicon.

5. One gramme of iron is converted into ferric chloride and the product is dissolved in water. What volume, at normal temperature and pressure, of hydrogen sulphide is theoretically required to completely reduce the ferric chloride to ferrous chloride?

6. Describe and explain a method for the exact determination of the amount of carbon dioxide in atmospheric air.

7. How is sulphur dioxide usually made on the small scale? How is it made by the vitriol-maker? How would you liquefy this gas, and what are the chief properties of the liquid?

8. Name the chief sources of silver and describe how the metal is obtained from argentiferous lead.

9. What substances, other than ozone, have the power of turning iodized starch-paper blue? How are they distinguished from ozone?

10. What reactions occur when the following pairs of substances dissolved in water are mixed together. (*a*) HCl and HNO_3; (*b*) HCl and $KClO_3$; (*c*) $NaHCO_3$ and $MgSO_4$; (*d*) SO_2 and I_2.

1892.

1. From what natural sources are potash compounds obtained? Describe the mode of manufacture of potassium iodide, potassium nitrate, and potassium bichromate.

2. State what happens when the following substances are heated to a sufficiently high temperature with charcoal: sulphur; phosphoric oxide; arsenious oxide; zinc oxide; litharge; sodium carbonate. Express the reactions in equations.

3. An unknown volume of hydrogen sulphide required 157 cb. c. of chlorine for complete decomposition. What was the volume of the hydrogen sulphide?

4. How is perchloric acid prepared and how is it distinguished from hypochlorous and chloric acids?

5. Describe two principal methods of obtaining copper and name its most important alloys.

6. How is hydriodic acid solution prepared? What happens when it is treated with (*a*) caustic potash; (*b*) chlorine; (*c*) starch-paste; (*d*) hydrogen dioxide? By what experimental methods can you show that hydriodic acid gas contains half its volume of hydrogen?

7. Give the systematic names and chemical formulae of the following minerals: fluorspar, iron pyrites, cinnabar, pyrolusite, haematite, heavy-spar, galena, felspar, selenite, calamine, calcspar, caelestine.

8. 0·369 gramme of aluminium liberated 0·04106 gramme of hydrogen on being dissolved in a strong solution of sodium hydrate. On the assumption that alumina is a sesquioxide, Al_2O_3, find from these data the atomic weight of aluminium.

9. How is hydrochloric acid made on the large scale, and how is it transformed directly or indirectly into bleaching powder and potassium chlorate?

10. Describe and explain the various methods of determining the amount of aqueous vapour in the air.

1893.

O = 16. N = 14. Ag = 108. Hg = 200. Fe = 56. Mn = 55.

1. Define "symbol," "formula," "atomic weight," "molecular weight."

Explain the relation of an equivalent to an atomic weight, and state the numerical value of the equivalents of oxygen, nitrogen, silver, and mercury.

2. How is nitric acid manufactured? What substances are found in nitric acid made on the large scale at the commencement and at the termination of the process, and what means are employed to purify the acid therefrom?

3. Give full and exact reasons for assigning the formulae O_2, O_3, P_4, Hg, and Cd to oxygen, ozone, phosphorus, mercury and cadmium.

4. Describe the properties of silica, and especially those of the soluble modification. By what means are insoluble silicates rendered soluble in water or in acids?

What do you understand by orthosilicic acid?

5. How is hydrogen dioxide prepared? What is its action upon silver oxide, manganic oxide, and potassium iodide?

6. What weight of hydrogen might be prepared by the action of a cwt. of iron nails upon steam in a red-hot tube, supposing the chemical change to be complete?

7. What is the composition of the substance known as white arsenic? What formula is erroneously assigned to it, and how has it been proved to be incorrect? Write constitutional formulae for arsenious and arsenic acids.

8. What metals would you consider to be most nearly allied with iron? Tabulate the chief characters of these metals and their more important compounds with a view to justify your answer.

9. Calculate the volume of chlorine, measured at 15° and 740 mm., obtainable by dissolution of 10 grammes of pure manganese dioxide in an excess of hydrochloric acid.

10. Give the common and systematic names and chemical formulae of the chief ores from which the metals, mercury, zinc, lead, tin, chromium, and manganese are obtained. Describe the production of zinc and of the metal which is commonly associated with it.

1894.

$H = 1$. $O = 16$. $C = 12$. $N = 14$.

1. What weight of air, free from aqueous vapour and carbon dioxide, and containing 23 per cent. by weight of oxygen, is needed to burn 1 ton of coal of the following percentage composition :—

Carbon	81·5
Hydrogen	5·0
Oxygen	5·2
Nitrogen	1·6
Ash consisting of fully oxidised substances ..	6·7
	100·0

2. State precisely what takes place when the following gases are passed over red hot copper turnings :—(*a*) oxygen, (*b*) hydrogen, (*c*) chlorine, (*d*) nitric oxide.

3. How is nitric acid manufactured? Describe and explain by equations the ordinary green vitriol test for nitric acid.

4. Under what conditions can the hypochlorite in bleaching powder be converted into chlorate? How is calcium chlorate converted into potassium chlorate on a large scale?

5. From what sources and in what manner is white arsenic obtained? The formula of arsenious acid is commonly written H_3AsO_3; what evidence exists in favour of this expression?

6. You are supplied with 500 grammes of washing soda crystals, with the object of making caustic soda therefrom. How would you proceed, and what weight of product would you expect to get?

7. The specific heat of a certain metal is ·031; what is approximately its atomic weight? What other facts would be required in order to establish its atomic weight with accuracy?

8. Starting from potassium dichromate, how would you obtain the following compounds of chromium :—CrO_3, Cr_2O_3, CrO_2Cl_2, $(NH_4)_2CrO_4$.

9. What are the causes of permanent and temporary "hardness" of natural waters, and what means have been proposed for softening excessively hard water? How would you test for lead in a sample of drinking water?

10. What facts have been discovered with reference to the vapour density of hydrofluoric acid, the action of an electric current upon the anhydrous liquid, and the conditions requisite for the isolation of the element fluorine.

1895.

$Ca = 40$. $C = 12$. $O = 16$.

1. Describe the effect of mixing a solution of bleaching powder with manganous sulphate, cobalt nitrate, sulphuric acid, sodium carbonate, and hydrogen peroxide, respectively.

2. Classify the common metals, mercury, copper, zinc, antimony, tin, gold, silver, platinum, lead, and iron, according to the action of nitric acid upon them.

3. What volume of dry carbon dioxide, measured at 12° C., and under a pressure of 755 mm., can 10 grammes of marble theoretically afford if completely decomposed by heat?

4. Describe any two methods by which you would test the validity of the expression NH_3 for ammonia gas.

5. Give examples of ferrous and ferric salts; point out their distinctive characters, as well as tests for them; describe and explain the methods by which they can be changed one into the other.

6. If the equivalent of magnesium by 12·1, explain fully how you would proceed in order to ascertain whether or not the equivalent and atomic weights are identical.

7. What is the method in general use for the preparation of bleaching powder? What is the composition of this substance? What is the action of water upon it? Why is it alkaline? What action has carbon dioxide on a solution of bleaching powder?

8. Describe the conversion of salt-cake into soda-ash, and the process of causticising the ash so as to yield solid caustic soda. State the impurities commonly occurring in the commercial article.

9. Arrange in parallel columns the formulae of the best known phosphates and arsenates in such manner as to show that they are closely analogous in composition, and state in what properties they resemble each other.

10. Describe the chief physical and chemical properties of aluminium. From what sources and by what processes is the commercial metal best obtained? Describe any useful alloys of this metal.

1896.

H = 1. N = 14. O = 16. S = 32.

1. Describe, without minute detail, the experiments you would make in order to ascertain whether the formula CO correctly represents the molecular composition of carbon monoxide gas.

2. The specific heat of copper is 0·0952; calculate from this datum the atomic weight of the metal, stating the general principle involved. Refer to any exceptions to this general principle.

3. By what means can each of the three phosphoric acids (hydrogen phosphates) be obtained, using common "phosphate of soda" as the primary material in each case?

Draw up a tabular statement of the reactions by which these acids are distinguished from one another.

4. Describe the preparation of a concentrated solution of hydrogen peroxide, and give equations showing the action upon this substance of (*a*) manganese dioxide, (*b*) silver oxide, (*c*) neutral solution of potassium permanganate, and (*d*) potassium permanganate acidified with sulphuric acid.

5. Describe any experiment which shows that ammonium chloride when vaporised undergoes dissociation.

6. What quantity of nitric acid and of sulphuric acid, respectively, would be required to neutralise 10 litres of ammonia gas dissolved in water?

The gas may be supposed to have been measured at 0° C. and 760 mm.

7. Explain the production of the gaseous hydrides of arsenic and antimony in the ordinary analytical tests for those elements; point out the distinctive characters of the hydrides, and explain the chemical changes which occur when each gas is led into a solution of silver nitrate.

8. How is lead extracted from the native sulphide, and obtained in a commercially pure condition?

9. Enumerate the metals which are capable of producing "alums." Write the formula of common alum, describe its usual crystalline form; and, being supplied with a sufficient quantity of the salt, state how you would proceed to make a specimen consisting of distinct crystals.

10. State the general characters of the magnesium-zinc-cadmium family of metals, and indicate their relations to the alkaline earths on the one hand and to aluminium on the other.

1897.

1. The formula H_2CO_3 is usually attributed to carbonic acid; upon what evidence is this based?

2. Chlorine gas is passed into the following solutions and mixtures; explain by equations, the effects produced in each case:—

(*a*) Cold solution of caustic potash.
(*b*) Hot solution of caustic potash.
(*c*) Bismuthic oxide suspended in solution of potash.
(*d*) Potassium iodate dissolved in solution of caustic potash.
(*e*) Solution of potassium iodide in water.
(*f*) Mixture of silica and carbon, red hot.

3. Give exact instructions for preparing, upon a small scale, any two of the following compounds:—pure crystallized copper sulphate, crystallized ferrous ammonium sulphate, chromium trioxide, chromyl chloride (CrO_2Cl_2), crystallized trisodic phosphate, crystallized antimony trichloride.

4. Describe the production of zinc by the Belgian process. What impurities are usually present in commercial zinc?

5. State the law of Dulong and Petit relating to specific heats. A certain element has the equivalent 40, and forms a volatile chloride the vapour density of which is about 113 ($H = 1$). What should the specific heat of the element be, approximately?

6. There are three oxides of lead which have the composition shown below:—

Pb	92·85	90·63	86·51	per cent.
O	7·15	9·37	13·49	per cent.
	100·00	100·00	100·00	

Illustrate the law of combination in multiple proportions, by reference to the composition of these three oxides.

7. Give examples of monatomic, diatomic, triatomic, and tetratomic molecules of elementary substances, and state how their constitution has beed arrived at.

8. Describe any process employed for extracting copper and silver from pyrites cinder (residue of vitriol manufacture).

9. What are the chief characteristics of the elements calcium, strontium, and barium, and the properties of their chlorides, oxides, and sulphates, which lead to their classification in one family or sub-group?

10. How would you prepare *pure* hydrogen sulphide, and what operations would you perform in order to establish the formula H_2S?

1. Write the formulae of the following compounds with their several proportions of water, if any, when crystallized :—alum, blue vitriol, Epsom salt, common sodium phosphate, microcosmic salt, sal ammoniac, white precipitate, corrosive sublimate.

2. Describe a good method for the exact determination of carbon dioxide in common air.

3. A solution of hydrogen iodide in water can be obtained by the interaction of hydrogen sulphide and iodine in presence of water, but when the solution contains about 50 per cent. of HI the action ceases. Explain this effect and state how a stronger solution may be obtained.

4. State the general characters of the metals of the alkaline earths. What is the relation of magnesium to this group?

5. How is potassium permanganate made? Write equations showing the action of this salt, acidified strongly with sulphuric acid, upon each of the following substances dissolved in water :—ferrous sulphate, potassium iodide, sodium peroxide, oxalic acid.

6. Describe the preparation, composition, and properties of silicon hydride.

7. What is spiegeleisen? For what purpose is it used? What is the difference between spiegeleisen and ferromanganese?

8. Give the names and formulae of the principle minerals which contain arsenic, and state how the element may be obtained from any one of them.

9. How has the vapour density of arsenic been determined, and what conclusion has been arrived at as to the constitution of the molecule of this element and of its common oxide?

10. What is gypsum? Describe the preparation of plaster of Paris. Explain the change which causes the setting of the plaster.

1898.

1. If you were provided with hydrochloric acid, manganese dioxide, and chalk, how many substances could you prepare? Write the formula of each, and show by an equation how it is formed?

2. Write the formulae of the following minerals :—iron pyrites, cinnabar, selenite, Iceland spar, galena, felspar, olivine, carnallite. By what treatment could you prepare pure silica from any of these substances?

3. State the "Law of Avogadro" and the facts upon which this hypothesis is based. Define the word *molecule* as used in connection with the law.

4. Describe the action of water under different conditions upon the several chlorides of phosphorus, arsenic, antimony and bismuth.

5. What are the chief natural sources of boron? Write the formula and describe the chief properties of its oxide, and state how you would prepare a specimen of its oxide.

6. A white substance held in the Bunsen flame imparts to it a green tinge. Name the elements whose compounds behave in this way, and state how you would distinguish between them.

7. How would you prepare chlorine and oxygen respectively from bleaching powder? Explain by equations in each case.

8. A metallic oxide when moistened with water becomes hot, and on addition of more water furnishes a strongly alkaline solution which gives a copious white precipitate with carbon dioxide. This precipitate is not appreciably affected by heating it to redness. What is this oxide and what changes has it undergone in these experiments?

9. By what experiment would you prove that hydrogen chloride contains half its volume of hydrogen?

10. A sample of bromine is known to contain a small quantity of chlorine; how would you purify it?

11. How would you prove that lime contains oxygen?

12. Give exact instructions for preparing upon a small scale any two of the following compounds:—pure sodium chloride (from common salt), crystallized ferrous ammonium sulphate, solution of ammonium hydrogen sulphide, crystallised microcosmic salt (sodium ammonium hydrogen phosphate).

1899.

1. What weight of sulphuric acid containing 98 per cent of H_2SO_4 would be required to decompose completely 250 grams of potassium nitrate in a glass retort?

2. What happens to phosphorus pentachloride when it is heated? Under what conditions can this compound give vapour having nearly the calculated density?

3. Give particulars of processes for the preparation of the following substances in a state of purity:—

(*a*) Crystallised silver nitrate from silver coins.

(*b*) Potassium nitrate from impure salt containing chloride.

(*c*) Orthoarsenic acid.

(*d*) Chromium trioxide.

4. How would you prove that hydrogen sulphide contains its own volume of hydrogen? Describe precisely how the experiments should be made.

5. Contrast the production and properties of perchloric and periodic acids.

6. Give an account of the preparation and properties of the compounds which nitrogen forms with hydrogen.

7. What is the composition of heavy spar and of witherite? How would you prepare from each a crystallised specimen of the corresponding metallic nitrate?

8. What is the action of ozone upon potassium iodide, and how would the effect be distinguished from that which is produced upon the same salt by nitrogen peroxide? Calculate the weight of potassium iodide equivalent to one gram-molecule of ozone.

$$K = 39{\cdot}1. \quad I = 126{\cdot}8. \quad O = 16.$$

9. Describe, with any necessary detail, the preparation of any three solid substances of definite composition, such as salts, oxides, etc., which you have made with your own hands.

10. Explain fully why the formula for the molecule of hydrogen is written H_2 and of oxygen O_2.

11. What is the action of water upon the following substances: red-hot iron, phosphorus, pentachloride, sulphuric anhydride, chromyl dichloride (CrO_2Cl_2), magnesium nitride, sodium dioxide? Give equations.

12. Give an account of the reduction of tin from its ore, and of the purification of the metal.

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