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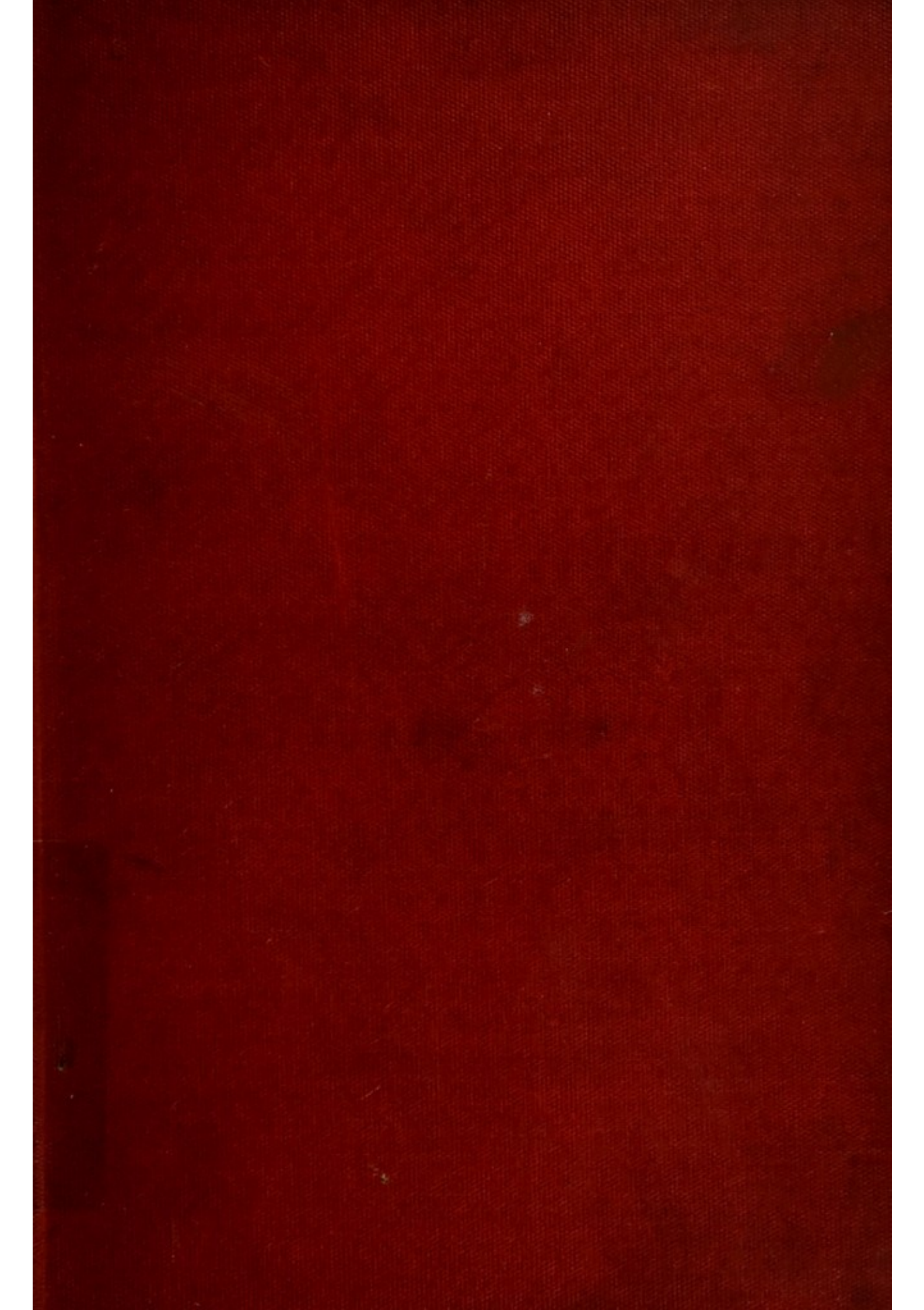
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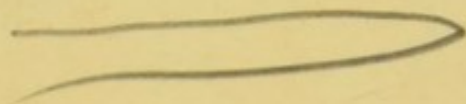
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AN INTRODUCTION
TO
CHEMICAL THEORY



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AN
INTRODUCTION
TO
CHEMICAL THEORY

BY
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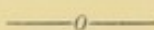


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PREFACE.



THOSE who have had to teach the elements of both Chemistry and Physics to the same classes of students usually find the progress of their pupils more rapid and satisfactory, for a time at least, in the latter subject. This is due in part to the smaller number of facts, apparently disconnected, which are required before they can be grouped together and simple theories built up deductively. This is further intensified by the fact that so many of the elementary text-books in chemistry are occupied too fully by the mere enumeration of facts and description of experiments, to the exclusion of the more philosophical parts of the subject. It is hoped that this small book may to some extent make up for this defect, and lead, on the part of those using it, to the desire for more knowledge of this most interesting branch of chemical science. Throughout it has been assumed that the student has a fair knowledge of chemical facts and experiments, and also, to a certain extent, that he may have the advantage of access to a teacher. For this reason references have frequently been made to matters somewhat outside the subject under discussion, for the pur-

pose of stimulating the more enquiring student, without at the same time perplexing those less so. On the other hand, many examples of reactions have been repeated in a way that those unacquainted with the difficulties and requirements of less brilliant students may be apt to think unnecessary.

It need hardly be remarked that no claim for either originality or completeness is claimed for such a work. As far as possible, all very debatable matter has been omitted, and it is for this reason, for example, that the account of the theories of solution has been made very short.

Finally, the author can but acknowledge his indebtedness to the published works of chemists in general, and especially to those of Lothar Meyer and of Ostwald, both of whom have done so much to encourage the study of Chemical Theory.

A. SCOTT.

CAMBRIDGE, *November* 1891.

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CHAPTER I.

ON THE CONSTITUTION OF MATTER.

FEW problems have as many attractions for ingenious speculators as that regarding the constitution of matter. We therefore find that it has been a subject of the theories of thinking men in all ages. Without going into a history of the various theories which have been propounded from time to time, we will consider only the one which has been built up by the labours of chemists and physicists on the results of experiment. It stands this test of a true theory, that it not only serves to explain all known facts, but has enabled many facts to be foreseen and demonstrated by experiment afterwards.

Matter is not divisible to *any* extent. There is a definite limit to which we come in the case of every substance. In fact, it is made up of various definite particles. If we take a piece of glass, for example, we can imagine it broken by mechanical means into very small pieces, and these again into still smaller pieces, till we come to the smallest piece of glass possible; this is called a *molecule* of glass. If we now adopt chemical means, we may break it up still further into three substances—soda, lime, and sand; and each of these we find we can again, by chemical means, break up into two

new substances—soda into a metal, *sodium*, and a gas, *oxygen*, the lime into a metal, *calcium*, and the same gas *oxygen*, and the sand into a brown powder, *silicon*, and again *oxygen*. These four new bodies—sodium, calcium, silicon, and oxygen—however, have hitherto resisted all attempts to break them up into new substances of a simpler nature. They belong to that class of bodies called elements, which are simply substances which have resisted all attempts to decompose them, but these may possibly be each one resolved into simpler substances again, when we have more powerful means of tearing them apart, or *analysing* them. We may prove sometimes also that a body is not a true element by building it up from simpler substances. We are then said to *synthesize* that substance from its elements.

Of elements at present we know about seventy, which, built together in more or less simple proportions, give rise to an almost infinite number of definite compounds.

If, then, we take any form of matter, and after applying both mechanical and chemical tests of every kind we can only find one kind of substance in it, we assume that we have got an elementary form of matter, and that all its ultimate particles are alike. These ultimate particles of elements are called *atoms*.

We may be unable by mechanical means (such as sifting, washing, or testing with a magnet or by using a microscope) to detect any diversity or want of homogeneity in a substance, yet may be able to do so by chemical means (such as treatment with acids, roasting alone or in presence of air or by the passage through it of a galvanic current), and separate it into two or more substances differing from the original substance, then, in

all probability we have got a chemical compound to deal with, all the *molecules* of which are the same, but the atoms of which these molecules are built up differ from one another. The atoms of the elements themselves are generally combined together into molecules at ordinary temperatures, each molecule usually consisting of two atoms. If by mechanical means alone we are able to detect more than one form of matter in any substance we may safely conclude we have a mixture, the molecules in which are not all the same.

A mixture, therefore, is a substance in which the molecules are not all of the same kind.

A compound is a substance of which the molecules are identical in every respect, but the atoms of which each molecule is built up are of different kinds.

An element is a substance of which the atoms are all alike.

The chemical and physical properties of gases indicate very clearly that matter in that form is in its simplest state of aggregation. According to the kinetic theory of gases developed by the splendid researches of Joule, Clausius, Clerk Maxwell, and others, a gas consists of particles moving with immense velocity, and the pressure exerted by a gas on the walls of the vessel containing it is due to the impact of these molecules. From it the three laws of Avogadro, Boyle, and Charles flow as necessary deductions. These three laws are :—

I. *Avogadro's Law*.—When two gases are at the same temperature and pressure the number of molecules in unit of volume is the same in both gases, and hence the densities of two gases are proportional to the masses of their individual molecules.

II. *Boyle's Law*.—The volume of any given mass of gas varies inversely as the pressure, the temperature remaining the same, or the product of the pressure and the volume of a given mass of any gas is a constant quantity.

III. *Charles' Law*.—All gases expand equally under equal increments of temperature; this rate is $\frac{1}{273}$ of its volume at 0° C. per degree centigrade. Or we may state it as "The volume of a given mass of every gas is proportional to its absolute temperature."

These three laws only hold strictly with a perfect gas. Avogadro's law can be tested by determining with accuracy the volumes in which gases combine together. In the case of hydrogen and oxygen it is very nearly in the proportion of two volumes of hydrogen to one of oxygen, but not rigidly so, the true ratio being 2.0024 to 1. That is, then, that the number of molecules in one volume of oxygen is to that in one volume of hydrogen as 10,012 to 10,000.

Coming to Boyle's law we see how this may be. We must remember that the effect of increase of pressure is to diminish the mean distance of the molecules and not to make the molecules themselves become smaller. The law can only hold, then, even with a perfect gas, when the volume of the molecules is as nothing to the distance between them. All gases which we know, however, yield to increase of pressure more than the law (as usually enunciated) requires, with the single exception of hydrogen, which does not yield quite enough.

This is noticeable even at comparatively low pressures, as the following measurements by Regnault show. He measured a volume of gas and its corresponding pressure,

then increased the pressure till the volume was reduced to exactly half the original.

For hydrogen :—

$$\begin{array}{lll} V_1=2 & P_1=2211\cdot18 & \frac{P_1V_1}{P_2V_2}=\frac{4422\cdot36}{4431\cdot14}=0\cdot998584 \\ V_2=1 & P_2=4431\cdot14 & \end{array}$$

and

$$\begin{array}{lll} V_1=2 & P_1=12513\cdot03 & \frac{P_1V_1}{P_2V_2}=\frac{25026\cdot06}{25076\cdot78}=0\cdot99473 \\ V_2=1 & P_2=25076\cdot78 & \end{array}$$

For nitrogen :—

$$\begin{array}{lll} V_1=2 & P_1=753\cdot96 & \frac{P_1V_1}{P_2V_2}=\frac{1507\cdot92}{1506\cdot24}=1\cdot001012 \\ V_2=1 & P_2=1506\cdot24 & \end{array}$$

and

$$\begin{array}{lll} V_1=2 & P_1=2159\cdot36 & \frac{P_1V_1}{P_2V_2}=\frac{4318\cdot72}{4311\cdot97}=1\cdot001097 \\ V_2=1 & P_2=4311\cdot97 & \end{array}$$

For carbon dioxide :—

$$\begin{array}{lll} V_1=2 & P_1=764\cdot03 & \frac{P_1V_1}{P_2V_2}=\frac{1528\cdot06}{1516\cdot00}=1\cdot007597 \\ V_2=1 & P_2=1516\cdot00 & \end{array}$$

and

$$\begin{array}{lll} V_1=2 & P_1=8393\cdot68 & \frac{P_1V_1}{P_2V_2}=\frac{16787\cdot36}{15493\cdot00}=1\cdot084278 \\ V_2=1 & P_2=15493\cdot00 & \end{array}$$

No gas, therefore, obeys Boyle's law perfectly, and their deviations from it are not the same in extent; hence this alone prevents Avogadro's law from being an absolute law.

Although at low pressures the product PV is too small, if the pressure be increased continuously it steadily diminishes to a minimum; then, again, increases till it surpasses its original value, as is shown by the following tables :—

COMPRESSIBILITY OF NITROGEN (Cailletet) :—

P m.	V	PV	T ° C.
39·359	207·93	8184	15·0
49·566	161·85	8022	14·9
59·462	132·86	7900	15·0
64·366	123·53	7951	15·0
69·367	115·50	8011	15·0
79·234	103·00	8162	15·1
109·199	77·70	8484	15·6
149·205	59·70	8907	16·5
181·985	51·27	9330	17·2

COMPRESSIBILITY OF AIR AT ORDINARY TEMPERATURES
(Amagat). From *Properties of Matter* (Tait).

Pressure in atmospheres.	PV
1	1·0000
31·67	·9880
59·53	·9815
73·03	·9804
84·21	·9806
94·94	·9814
133·51	·9905
176·17	1·0113
282·29	1·0837
400·05	1·1897

Hence at ordinary temperatures, and at 152·3 atmospheric pressure, air is reduced to $\frac{1}{152\cdot3}$ of its volume.

The reason of this is plain. Suppose that at a given pressure the volume of 1 litre is occupied by a quantity of gas, the volume of the molecules of which equals 1 c.c., we will then have 999 c.c. unoccupied volume ; doubling the pressure we reduce it to

$$\frac{999}{2} + 1 = 499\cdot5 + 1 \text{ c.c.} = 500\cdot5 = V$$

$$PV = 2 \times 500\cdot5 = 1001$$

and for ten atmospheres pressure

$$\frac{999}{10} + 1 = 99.9 + 1 \text{ c.c.} = 100.9 = V$$

$$V = 10 \times 100.9 = 1009$$

This then resembles the behaviour of hydrogen, in which PV is too great even from low pressures. If, however, the increase of pressure causes too great a diminution, it is evident that we are multiplying each time the volume of the molecules by larger and larger numbers, and that in time, when the number becomes high enough, it will more than make up for the too great diminution of the distance between the molecules.

As oxygen is then more compressible than it ought to be, according to Boyle's law, the higher the pressure the more also must it deviate from Avogadro's law; and, consequently, at ordinary pressures it is highly probable that it even then contains more molecules than an equal volume of hydrogen under the same conditions.

Charles' law in like manner is not obeyed by the gases with which we are acquainted. According to the kinetic theory of gases, we have seen that all gases ought to expand at an equal rate with one another, and for equal increments of temperature (say from -10°C. to $+10^{\circ}\text{C.}$, and from 80°C. to 100°C.) a given mass ought to increase in volume equally.

As with Boyle's law, it is those gases which are most easily liquefied which deviate most.

COEFFICIENTS OF EXPANSION BETWEEN 0° AND 100°C.

	Constant pressure of 760 mm.	Constant volume.
Hydrogen,	·003661	·003668
Air,	·003670	·003665
Carbon monoxide,	·003669	·003667
Carbon dioxide,	·003710	·003686
Sulphur dioxide,	·003903	·003845

Again, we see that hydrogen behaves in a contrary way to the other gases, its coefficient under constant volume being greater than under constant pressure, while it is less in all the others.

In a liquid the particles are more or less kept together by cohesion, and roll over one another rather than move about freely. The condition of a liquid mass at ordinary temperatures may be compared to peas in a box, which take an approximately level surface, with the addition that each is moving with a velocity depending on the nature of the molecule and on its temperature. The higher the temperature the more energetic the motion, and some particles near the surface, as it were, escape into the space above, and thus we account for evaporation.

In a solid the particles only vibrate about a mean position until by increase of temperature this vibration becomes so great that the particles become free from one another when we get a liquid.

With the internal motion of a solid we have little to do in chemistry, but we do utilise the different rates of motion in the molecules of liquids and of gases.

First, we may readily prove that the particles of gases move rapidly at ordinary temperatures.

Take a cylindrical porous jar, such as is used in a galvanic battery; close the open end with an india-rubber stopper having a narrow glass tube through it, and by means of an india-rubber tube connect the jar with a manometer. As long as air is inside and outside (temperature being the same) no change will be visible (though it does not follow that no changes are going on). Place now the porous jar in a vessel full of

hydrogen gas, when at once a large increase of pressure inside the jar will be indicated. Something must have got into the jar to have thus increased the pressure. If, instead of putting the jar into hydrogen, we had put it into carbon dioxide, we would have had a diminution of pressure instead of an increase. Something, therefore, must have got out of the jar in this case.

Priestley had observed that even when the pressure inside vessels of unglazed earthenware was greater than that of the surrounding atmosphere, gases from the fuel he was employing to heat them would find their way inside. Döbereiner had also observed that hydrogen enclosed in a cracked jar over water gradually escaped, and the water inside rose considerably above the surface of that in the pneumatic trough.

Dalton made many experiments of a simple nature on diffusion of gases. One was to take two flasks and connect them by means of two corks and a long and narrow glass tube; fill one with hydrogen and the other with a denser gas, as oxygen or carbon dioxide. He showed that, no matter what the gases were, even when the hydrogen flask was directly above the one containing the denser gas, the two gases always tended to mix completely. Berthollet further showed that it required a much longer time for mixture when the lighter gas was oxygen, nitrogen, or air, instead of hydrogen. But it is to Graham that we are indebted for the first accurate experiments on the subject. He first showed that when hydrogen escaped, as in Döbereiner's observation, at the same time a certain quantity of air entered.

He showed that the rates at which various gases pass

through unglazed earthenware, or a plate of compressed graphite, were inversely proportional to the square roots of their density. Some of his numbers are given in the following table :—

	Density air = 1.	$\frac{1}{\sqrt{\text{Density}}}$	Volume of gas escaping for 1 of air entering.
Hydrogen,	·069	3·779	3·83
Marsh gas,	·554	1·337	1·344
Carbon monoxide,	·968	1·016	1·015
Nitrogen,	·971	1·015	1·014
Ethylene,	·978	1·011	1·019
Oxygen,	1·106	·951	·949
Nitrous oxide,	1·527	·809	·820
Carbon dioxide,	1·529	·809	·812

But, according to the kinetic theory of gases, we have $M_1 V_1^2 = M_2 V_2^2$ when we have two gases in thermal equilibrium, M_1 and M_2 being the masses of their molecules, and V_1 and V_2 their respective velocities,

$$\therefore \frac{M_1}{M_2} = \frac{V_2^2}{V_1^2} \text{ and } \sqrt{\frac{M_1}{M_2}} = \frac{V_2}{V_1}.$$

This is what Graham proved by experiment, viz., that the velocity of the molecules is inversely as the square roots of their masses.

As the masses of the molecules of hydriodic acid (HI), oxygen (O_2), and hydrogen (H_2) are to one another as 128 : 32 : 2, or as 64 : 16 : 1, the velocities of their molecules must be as

$$\frac{1}{\sqrt{64}} : \frac{1}{\sqrt{16}} : 1 = \frac{1}{8} : \frac{1}{4} : 1, \text{ or as } 1 : 2 : 8.$$

It is easy to calculate the velocity of the particles of a gas, as has been shown by Joule, if we know the

total mass of the gas and the pressure it exerts. At 0° C. it is for

Hydrogen,	1844 metres per second.
Oxygen,	461 " "
Nitrogen,	492 " "
Carbon monoxide, . . .	493 " "
Carbon dioxide, . . .	391 " "

All gases, as far as we know, mix perfectly with one another, but it is not so with liquids, as oil and water, or water and mercury, which will not mix however long they may be left together, and even if thoroughly shaken together will again separate into two layers. Graham, however, showed that if we take two liquids of different densities which will mix, and place the denser one below the lighter one, the denser one will mount through the lighter one, which in turn will find its way down. This is readily seen by taking one of them highly coloured, as a saturated solution of potassium bichromate for the denser one, and water alone for the lighter. The colour will be seen gradually to diffuse upwards through the whole mass of liquid.

The method of experimenting adopted by Graham was to take a bottle or jar with a neck contracted somewhat, and fill it to within half an inch of the top with the solution of the salt to be investigated; then fill it completely with pure water, and having covered it with a glass plate, carefully place the whole in a larger jar containing pure water; then remove the glass plate and allow the diffusion to go on in a cellar where the temperature is nearly constant. After a given time the salt which had diffused out was estimated either by evaporating the water in the outer jar to dryness, or by some chemical method depending on the nature of the salt.

Some of the conclusions which he arrived at are :—

1. That different salts in solutions of equal strength diffuse unequally in equal times.
2. With each salt the rate of diffusion increases with the temperature, and at any given temperature is proportional to the strength of the solution, at least when it does not contain more than 4 or 5 per cent.
3. That there exist classes of equi-diffusive substances which coincide in many cases with isomorphous groups. We have the same rate for hydrochloric, hydrobromic, and hydriodic acid ; for barium, strontium, and calcium nitrates, &c.

The general law regulating these movements seems to be that the velocity with which a soluble salt diffuses from a stronger into a weaker solution is proportional to the difference of concentration between two contiguous strata.

Bodies which crystallise readily as a rule diffuse far more rapidly than substances of an uncrystallisable nature, such as glue ; and on this is based a method of separating bodies having very different diffusion rates from one another. Graham named these two classes crystalloids and colloids, and the method of separation, *dialysis*. The times of equal diffusion of several substances are given in the following table :—

Hydrochloric acid,	1
Sodium chloride,	2·33
Sugar,	7
Magnesium sulphate,	7
Albumen,	49
Caramel,	98

We see here that the molecules having greater masses

move more slowly than those with smaller. In applying dialysis to the separation of unequally diffusible substances, a tray-shaped vessel is made of parchment paper, supported by a ring of glass, and in it is placed the mixture, and the whole is supported or made to float on pure water. The crystalloids will pass rapidly through into the pure water, and as it gets more and more of them they will pass back again. The mixture will continue to lose them till the water outside is practically of the same strength as that inside. Hence the outside water ought to be repeatedly changed if we want to remove the whole of the crystalloids from the colloids. The best way is to support the dish in a stream, so that the crystalloids, having come through, are taken away and prevented from returning. In this way the mixture of hydrochloric acid, sodium chloride, and silicic acid formed by pouring a solution of sodium silicate into excess of hydrochloric acid, can in a few days give a solution of silicic acid, which will give no precipitate with silver nitrate. A solution of ferric chloride placed in the dialyser (or tray) can be separated completely into hydrochloric acid and ferric hydrate, which remains in the dialyser in a soluble form, the acid passing through.

Diffusion of gases has also been applied in analysis for the separation of mixed gases, under the name of *atmolysis*. If the mixture of hydrogen and oxygen from the electrolysis of water be passed through the stem of a long clay pipe, the gas issuing from it will be found to contain almost no hydrogen. Ordinary analysis is unable to detect a mixture of equal volumes of hydrogen and ethane (C_2H_6) from marsh gas (CH_4), as it has the same percentage composition and the same density. But if

we take two tubes of equal length, one of porous earthenware and the other of glass of larger diameter, and fit them together like a Liebig's condenser, and maintain a current of carbon dioxide through the annular space while the mixture of ethane and hydrogen is passed through the porous tube, the hydrogen with a little ethane will pass into the carbon dioxide, from which it may be separated by passing through potassium hydrate solution, the mixture from the inner tube may be similarly freed from carbon dioxide, and will be a mixture of ethane with a little hydrogen.

Apparently in exactly the same way as the gases from the burning fuel found their way into Priestley's earthenware vessels, carbon monoxide and hydrogen pass through certain metals, especially iron and platinum, at a red heat. However, on investigation it was soon seen that there was a connection between the metal and the gas which passed through, and that it had no relation to the general physical properties of the gas. What was necessary was a gas and a metal which would either combine with it, or at least absorb or *occlude* it, as it is termed. Carbon monoxide is readily absorbed and retained by metallic iron, although no definite compound has been detected, as has just been shown to be the case with nickel, with which it unites directly to form a liquid having the formula $\text{Ni}(\text{CO})_4$,* which readily breaks up again into the gas and metal at 180°C . If we take an iron tube, closed at one end and connected at the other with a Sprengel mercury pump, and exhaust completely, the

* A corresponding volatile compound of iron and carbon monoxide has now been discovered also.

vacuum remains as long as the tube is cold, but if raised to a red heat in a gas flame it is easy to pump out of the tube large quantities of carbon monoxide and hydrogen. Platinum readily permits of the passage of hydrogen through it, hence it is unsafe to ignite readily reducible materials in a platinum crucible, even although a strongly oxidising flame be used, as such always contains free hydrogen, which would find its way inside the crucible although the oxygen and nitrogen might not.

Graham also showed that the gases which come into a vacuum from the atmosphere through a very thin film of india-rubber suitably supported, contain a far larger proportion of oxygen than that in the atmosphere, the gas being so rich in oxygen that it readily relights a glowing splinter of wood. In the case of carbon monoxide and iron, platinum and hydrogen, and india-rubber and oxygen, we seem to have a solution of the gas in the solid; and just as an ordinary solution of a gas gives off that gas into a vacuum (or other gas free from it), so the iron gives off its carbon monoxide and the india-rubber its oxygen. The solution of gases in liquids which do not act chemically upon them depends definitely on the temperature and the pressure, and can be expressed by a simple law, to which we have no parallel in the cases of solubility of liquids and solids. It was known to many of the older observers, and was pointed out by both Cavendish and Priestley, that an increased pressure increased the quantity of gas dissolved, but the law was not clearly stated till 1803, when it was enunciated thus by Henry:—"Under equal circumstances of temperature water takes up in all cases the same volume of con-

densed gas as of gas under ordinary pressure. But as the spaces occupied by every gas are inversely as the compressing force, it follows that water takes up of gas, compressed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, &c., the volume absorbed under the common pressure of the atmosphere." If, however, the liquid be exposed to a mixture of two gases, it is found that the amount of each gas dissolved is in no case as much as it would have taken had each gas been presented to it alone at the total pressure, but that it takes up the quantities required by Henry's law if we take the partial pressures due to each gas separately.

An example will make this plainer.

Taking air as composed of 4 vols. of nitrogen to 1 vol. of oxygen, and the coefficient of solubility of oxygen as .04114 at 0° C. and of nitrogen .02035, 100 c.c. of water would dissolve of oxygen at the atmospheric pressure 4.114 c.c. of oxygen, and likewise of nitrogen 2.035 c.c., but the pressure of the oxygen is only $\frac{1}{5}$ of an atmosphere, therefore we have dissolved of oxygen $\frac{4.114}{5} = .823$ c.c., and the pressure of the nitrogen being $\frac{4}{5}$ of an atmosphere, we have of it $\frac{2.035 \times 4}{5} = 1.628$ c.c. The gases are then dissolved in almost exactly the proportions of 2 vols. of nitrogen to 1 vol. of oxygen, instead of 4 : 1. This is one of the best proofs that the air is a mixture and not a compound.

The above extension of Henry's law was discovered by Dalton, but not placed on a thoroughly sound basis till taken up by Bunsen and his pupils, who determined

with accuracy the coefficients of solubility of several gases in water and alcohol at different temperatures.

In the case of gases the amount dissolved is less the higher the temperature, and at the boiling-point none remains in solution or would be taken up. Hence, to ensure the freedom of water from dissolved gases, it is usual to boil it for some time.

If we have chemical combination between the liquid and the gas, then we will be unable to boil out all the gas. If we take the strongest hydrochloric acid solution and heat it, it will give off hydrochloric acid gas at first, but after heating for some time the percentage composition of the vapours given off is exactly the same as that of the liquid remaining behind in the retort, and both will remain so till the whole has been distilled. If we begin with it very weak the same point is reached, water distilling over first. The boiling-point gradually rises to 110°C. , when the liquid has exactly the same composition as when the experiment was begun with the strong solution of the acid. It corresponds to about 20 per cent. of hydrochloric acid, and almost to a hydrate, $\text{HCl} + 8\text{H}_2\text{O}$.

Ammonia, which is also a very soluble gas, behaves in an entirely different manner. When its solution is heated the gas comes off, accompanied by more or less steam, until all the ammonia is expelled, when pure steam comes off alone, pure water remaining in the retort. It is therefore easy to show that a neutral solution of ammonium chloride consists, in part at least, of hydrochloric acid and of ammonia, for on boiling it for a very short time it becomes distinctly acid in its reaction, as may be proved by adding litmus solution before boiling.

That water at its boiling-point should dissolve no gas might be anticipated, as its vapour tension alone equals that of the atmosphere; and also that as its temperature, and therefore its vapour tension increases, the rate of solubility should diminish, but this diminishes at a much greater rate than that of the increase of tension.

With regard to the solubility of solids in liquids, as a rule the amount of solid dissolved increases with increase of the temperature of the solvent. In the case of common salt the temperature makes but little difference, and many salts of calcium are more soluble at low than high temperatures, *e.g.*, the citrate, whilst several salts have temperatures of maximum solubility, so that a liquid saturated at a certain temperature deposits the salt on further heating, as is the case with many sulphates, notably that of sodium.

CHAPTER II.

ATOMIC WEIGHTS.

THE instrument of the chemist, *par excellence*, is the balance, and until this was recognised true chemistry made little real progress. Not but that the alchemists had weighed their components and then their products, but that true chemists never lose sight of any of the products, but endeavour to account at the end of the experiment for all the matter which they had at the commencement. One of the earliest researches of this kind, as remarkable for its clear and concise reasoning as its simple and accurate experiments, is that published in 1777, and entitled, *Experiments upon Magnesia Alba, Quicklime, and other Alkaline Substances*, by Joseph Black, M.D., Professor of Chemistry in the University of Edinburgh. From this time chemistry made rapid strides. By means of the balance alone could it be proved that matter was quite indestructible by any process at our command just as much as it is uncreatable. Chemical compounds were shown to have a definite composition, which accounted for their constancy in properties. Matter does not disappear in reality, although it may seem to do so—as in the case of a candle burning—for if we collect the products of the combustion by means of solid caustic soda, we find that these products weigh more than the candle which has dis-

appeared. The increase, however, was again shown to be at the expense of the atmosphere in which the candle burnt. The brilliant and conclusive experiments of Lavoisier on the relation of the air to combustion and oxidation, did much to lay the foundations of modern chemistry and gave a rational explanation of multitudes of undoubted facts which had been gathered together by the older experimenters in chemistry and alchemy.

Although carbon burning in oxygen gives rise chiefly to one gas, known now as carbon dioxide or carbonic acid gas, it is possible to obtain another gas, carbon monoxide or carbonic oxide, also containing only carbon and oxygen. These two gases have properties quite distinct from one another. The first is denser than air, extinguishes a burning candle inserted into it, does not burn, renders lime-water milky, while the other is a little lighter than air, and although it extinguishes a lighted candle inserted into it, itself takes fire at its surface exposed to the air; it does not turn lime-water milky, but the products of its combustion do so.

The percentage composition of these two gases was represented respectively as 27 parts of carbon to 73 of oxygen, and 43 parts of carbon to 57 of oxygen. No simple relation between the two gases is easily recognisable when presented thus, but if we consider how much oxygen is combined with one part of carbon, we find in the first 1 of carbon united to $2\frac{2}{3}$ of oxygen, and in the second 1 of carbon to $1\frac{1}{3}$ of oxygen. In fact, the one gas contains twice as much oxygen as the other combined to the same amount of carbon. Dalton also showed that olefiant gas or ethylene contained twice as much carbon united to the same quantity of hydrogen

as in marsh gas. The explanation which he gave of these facts was a revival of the atomic theory of the Greek philosophers, based now on experiment and not on speculation. Every atom of any one element was supposed to be identical in all respects, but to differ from those of all other elements especially in its mass. Dalton said that carbon dioxide was formed by the union of one particle of carbon with two particles of oxygen, and that carbon monoxide similarly consisted of one particle of carbon attached to only one of oxygen. Marsh gas he represented as two of hydrogen and one of carbon, and olefiant gas as one of each.

Not only did Dalton assume that matter was composed of atoms, and use this hypothesis to explain the composition of chemical compounds, but he proceeded to determine the relative masses of these reacting particles. In an appendix to a paper read before the Literary and Philosophical Society of Manchester on October 21, 1803, but not published till November 1805, he gave the following table :—

Table of the Relative Weights of the Ultimate Particles of Gaseous and other Bodies.

Hydrogen, 1	Nitrous oxide, . . . 13·7
Azote, 4·2	Sulphur, 14·4
Carbon, 4·3	Nitric acid, 15·2
Ammonia, 5·2	Sulphuretted hydrogen, 15·4
Oxygen, 5·5	Carbonic acid, . . . 15·3
Water, 6·5	Alcohol, 15·1
Phosphorus, . . . 7·2	Sulphurous acid, . . 19·9
Phosphuretted hydrogen, 8·2	Sulphuric acid, . . . 25·4
Nitrous gas, . . . 9·3	Carburetted hydrogen, 6·3
Ether, 9·6	Olefiant gas, 5·3
Gaseous oxide of carbon, 9·8	

Dalton further introduced a symbolic notation, not unlike that which we use so much, especially in organic chemistry. He represented—

Hydrogen,	⊙	Olefiant gas,	● ⊙
Oxygen,	○	Carbon monoxide,	● ○
Carbon,	●	Ammonia,	⊕ ⊙
Nitrogen or Azote,	⊕	Carbon dioxide,	○ ● ○
Water,	○ ○	Marsh gas,	⊙ ● ⊙

Dalton was continually changing his table of atomic weights as first published, as more and more accurate experiments were executed. Not only, however, are the numbers given by Dalton not exactly what we now take as the atomic weight, but it is evident we use multiples of them, as in the case of nitrogen, where we use approximately three times his number, representing ammonia as NH_3 , whereas he represented it practically as NH . The two represent the same relative composition, allowing for the want of accuracy of the older experiments, for ⊕ should have been equal to 4·6, and not to 4·2.

We must therefore inquire into the methods which give us the most trustworthy data for the measurements of the relative masses of the ultimate particles of matter which we term *atoms*.

Quite apart from its theoretical bearings, the accurate determination of the atomic weights of all the commonly occurring elements is one of very great practical importance, since in commercial analysis of every kind we determine the amount of an element or compound present in a mixture by converting it, as a rule, into some other compound of a very definite nature, which can be produced free from the other substances originally pre-

sent. To know the exact composition of the new compound the atomic weights of its constituents must be known with accuracy as well as those of the substance which is being estimated. These atomic weights must be all referred to one standard substance which ought to be of such a nature that all the others can be directly compared with it. For this reason, undoubtedly, oxygen is the substance best fitted for the standard. Still more do the philosophical and speculative problems, such as the possibility of resolving all kinds of matter into that of one primordial kind, and the endeavour to correlate the physical and chemical properties of the atoms with their masses, demand an estimation of these masses with the highest accuracy which we can attain.

We have already shown that the laws of Boyle and Charles, and consequently that of Avogadro, are only true to a limited extent, and that they are by no means mathematically exact. "Is this so with all the laws relating to chemical composition and constitution?" becomes an interesting question.

One of the first points which struck the early chemists in connection with chemical compounds was that of apparent fixity of composition. Not only, however, in their composition, but also a definiteness in the proportions in which they decomposed and reacted with one another was likewise observed. The substances especially studied were salts of various kinds. Homberg seems to have been the first who endeavoured to determine their composition by saturating the various bases with acids. His experiments, although far from accurate (since he used the carbonate and not the base itself, as Black pointed out), are perhaps the earliest

experiments in quantitative chemistry. Far more accurate were the experiments and reasoning of Wenzel, who was much struck by the fact that when two neutral salts mutually decompose one another the products remain neutral. He not only explained this, but proved by experiment that his explanation was the true one, viz., that the quantities of all the alkalis and alkaline earths required for neutralisation bear the same ratio for each of the acids. Thus, if equal quantities of any one acid be saturated respectively by 9.75 of barytes, 6.5 of strontia, 6 of potash, 4 of soda, 3.5 of lime, and 2.5 of magnesia, then if equal quantities of any other acid be taken and saturated in turn by each of these bases, the amounts required will be in exactly the same ratios. Fifteen years later Richter published practically the same views, although his experiments were not so accurate as those of Wenzel, nor did they attract any more attention until they fell under the notice of Berthollet and of Berzelius; the latter of whom being much struck with the analyses and the reasoning, undertook a series of experiments on the composition of salts to test rigorously the views set forth by Richter. While he was engaged in this research, Davy discovered the metallic constituents of the alkalis and alkaline earths, Dalton enunciated his Atomic Theory, and Gay Lussac published his Law of Volumes.

Berzelius improved the methods of analysis so much that very many of his results are quite equal to those of the present day, and it is to him that we are indebted for the first really accurate determinations of atomic weights.

The first determinations of this kind were more strictly termed "combining weights," or equivalent

weights, that is, the amount which will combine with or replace unit weight of some selected standard substance, usually oxygen or hydrogen.

Dalton adopted hydrogen as his standard, and it is still the usual unit adopted. Berzelius took as his standard substance, oxygen, making $O = 100$. In many books we find atomic weights referred both to oxygen and to hydrogen, those referred to the latter unit being *nearly* 16 times those referred to the former. The first step in every case is to determine with great accuracy the *equivalent* of the element which is the quantity required to combine with or replace one part by weight of hydrogen (or 8 parts of oxygen). The equivalent depends on no atomic theory, and its use is still adhered to by some chemists, especially in France.

But we may have an element combining with hydrogen or with oxygen in more than one proportion, as we have already seen with regard to carbon. In marsh gas we have 3 parts of carbon combined with 1 part of hydrogen, and in olefiant gas we have 6 parts of carbon combined with 1 part of hydrogen. Again, in carbon dioxide we have 3 parts of carbon combined with 8 parts of oxygen, and in carbon monoxide 6 parts of carbon with 8 parts of oxygen. We have to decide then between 3 and 6 as equivalents, and it may be that neither of them will be eventually adopted as the atomic weight. That number is either the equivalent itself or some multiple of it.

We will, before proceeding further, take some other examples of equivalents.

In hydrochloric acid we have 1 part of hydrogen united with $35\frac{1}{2}$ parts of chlorine.

. . . The equivalent of chlorine is 35.5.

In nine parts of water we have 1 part of hydrogen united to 8 parts of oxygen.

. . . The equivalent of oxygen is 8.

In seventeen parts of ammonia we have 3 parts of hydrogen united with 14 parts of nitrogen.

. . . The equivalent of nitrogen is 4.6.

In twenty-two parts of nitrous oxide we have 8 parts of oxygen united to 14 of nitrogen.

. . . The equivalent of nitrogen is 14.

In thirteen parts of benzene we have 1 part of hydrogen united to 12 parts of carbon.

. . . The equivalent of carbon is 12.

We have already seen that it is 3 and 6 in other compounds.

In 127 parts of ferrous chloride we have 56 parts of iron united to 71 parts of chlorine.

. . . The equivalent of iron is 28.

In 325 parts of ferric chloride we have 112 parts of iron united to 213 parts of chlorine.

. . . The equivalent of iron is 18.6.

It is quite apparent, then, that we may have many equivalents for one and the same element, but we can only have one atomic weight if the ultimate particles which we call atoms be a reality.

We may define an atom *to be the smallest quantity of an element which exists in a molecule of any of its compounds.*

Now, by Avogadro's law, as pointed out (page 3), we can readily determine the relative masses of the molecules of all compounds and elements which can be made to assume the gaseous condition without undergoing

decomposition. The densities of the vapours are exactly proportional to the molecular weights.

The methods of determining vapour densities may be divided into two classes :—I. *Those in which we measure the volume of vapour given by a quantity of substance previously weighed.* II. *Those in which we weigh the amount of substance in a previously fixed volume.*

To the former class belong the methods of Gay Lussac, Hofmann, and Victor Meyer, and to the latter that of Dumas. The advantage of Hofmann's method is that it is done under diminished pressure, giving thus a larger volume and requiring a lower temperature than if done under atmospheric pressure. V. Meyer's method, however, is by far the most convenient for chemical purposes, as we may use it up to any temperature that our vessels will stand, and the only temperature we require to determine is that of the evolved gas when measured.

For experimental details, books on physics and experimental chemistry must be consulted.

We have now to determine the relation between the atom and the molecule of hydrogen.

At 0° C. and at 760 mm. pressure a litre of hydrogen weighs .0898 gm., and a litre of hydrochloric acid, 1.6333 gm. A molecule of hydrochloric acid must then weigh $\frac{16333}{898} = 18.188$ times as much as a molecule of hydrogen.

18.188 parts by weight of hydrochloric acid when analysed are found to consist of .5 of hydrogen united to 17.688 of chlorine.

Therefore the amount containing unit weight of

hydrogen must be twice this or 36·376, which is the smallest number we can adopt for the molecular weight of hydrochloric acid, and as its molecule is 18·188 times as dense as that of hydrogen the molecular weight of hydrogen must be $\frac{36\cdot376}{18\cdot188} = 2$ when its atom is 1.

The same conclusion is arrived at by considering the synthesis of hydrochloric acid from its elements. 1 litre of hydrogen unites with 1 litre of chlorine to form 2 litres of hydrochloric acid. Let us assume that we are working under such conditions of temperature and pressure that the number of molecules in a litre is exactly one million, then it follows that one million of hydrogen molecules unite with one million of chlorine molecules to form two millions of those of hydrochloric acid, every one of which contains both hydrogen and chlorine—that is, one million of hydrogen molecules gives rise to two millions of molecules of hydrochloric acid, each of which contains hydrogen and chlorine, and at least an atom of each. A molecule of hydrogen must then be divisible into two parts, and therefore must contain at least two atoms. Similarly, it is clear that the chlorine molecule must contain two atoms.

We have no reason for supposing any more complex constitution for the molecule than the above; indeed, many other facts point to 2 as being the most likely number of atoms in the molecule. The density of hydrogen being 1, and its molecular weight 2, and the densities of gases being proportional to the masses of their molecules, we see why it is that the molecular weight is always equal to the vapour density (referred

to hydrogen as unity) multiplied by 2. If we have the specific gravity of the gas or vapour referred to air, we must multiply by 14.4×2 (the density of air referred to hydrogen being 14.4). Hence, for all those elements whose molecules consist of two atoms, the vapour density is represented by the same number as the atomic weight.

At high temperatures many of the molecules of the elements are more or less broken up into the individual atoms.

The molecule of sulphur at comparatively low temperatures, as 500°C ., consists of six atoms. Its vapour density referred to hydrogen is 96, therefore its molecular weight is 192. But hydrosulphuric acid has a density of 17, and therefore a molecular weight of 34. 34 parts contain 32 parts of sulphur united to 2 of hydrogen, therefore the atomic weight of sulphur cannot exceed 32, whence the molecule of sulphur at 500°C . must contain at least $\frac{192}{32} = 6$ atoms.

Similarly, on raising its vapour to much higher temperatures, it undergoes enormous expansion, and about 1200°C . its vapour is only 32 times the density of hydrogen at the same temperature and pressure; its molecular weight is then only 64, and the molecule consists of two atoms. Mercury vapour has a density of 100, and hence its molecular weight must be 200, but the molecules of all mercury compounds contain at least 200 parts of mercury; therefore here we have the atom and the molecule the same.

Phosphorus at comparatively low temperatures has a vapour density of 62 and molecular weight of 124. Its

atomic weight is not more than 31, for phosphuretted hydrogen has a density of 17 and molecular weight of 34, 34 parts by weight containing 3 parts of hydrogen and 31 of phosphorus. Its molecule, therefore, contains four atoms, although at high temperatures, about 1600°C ., it seems, according to Meyer and Biltz, to have only two.

If, however, we have no compound of an element which can be volatilised without decomposition, we must fall back on some other method of deciding what multiple of the equivalent is to be adopted as the atomic weight. Dulong and Petit discovered that elements of which the atomic weight was high had a correspondingly low specific heat, and that the one was inversely proportional to the other to a fair degree of accuracy. In other words, the product of the atomic weight and the specific heat yielded a constant number. Or as they expressed it, "the capacity for heat was the same for the atoms of all the elements."

This constant product is *about* 6.4.

The equivalent of zinc is 32.5; its atomic weight is then either 32.5, 65, 97.5, or 130; its specific heat is 0.931.

$$32.5 \times 0.931 = 3.02$$

$$65 \times 0.931 = 6.05$$

$$97.5 \times 0.931 = 9.08$$

65 is therefore the number to be taken as the atomic weight.

Again, potassium has an equivalent of 39, and a specific heat of .1655.

$$39 \times .1655 = 6.45$$

whence 39 is evidently the atomic weight.

Before considering the chief methods which have been adopted for the determination of the atomic weights of several of the commoner and more important elements, we must refer to a remarkable paper, published in 1815, entitled, "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms," by Dr William Prout, for it is due to it in no small degree, and to the controversies which have arisen from it, that we owe many masterpieces of experimental work. We have already seen what the relation is which exists between the atomic weight and the vapour density of some of the elements; but what Prout especially pointed out, and what has given rise to so much research is, that in the table which he gave of the atomic weights of fourteen elements, every one may be regarded as a multiple of that of hydrogen by a whole number. When more accurate experiments were made, however, it was proved that this would not hold in every case, especially that of chlorine, which is almost exactly $35\frac{1}{2}$ times that of hydrogen. Prout's law, as it was called, originally ran thus:—The atomic weights of all the elements are multiples of that of hydrogen. As circumstances arose which proved conclusively that this was untenable, Dumas modified it so that half and quarter multiples of the atomic weight of hydrogen were recognised. There is at present such a strong array of facts against it that it is in no sense a law, although much may be said in favour of some modification of it, such as the $\frac{1}{16}$ part of the atomic weight of oxygen being substituted for the atomic weight of hydrogen. We shall be more in a position to realise this when we have considered the determinations of the atomic weights themselves.

The famous researches of Professor J. S. Stas of Brussels, entitled, *Nouvelles Recherches sur les lois des proportions chimiques, sur les poids atomiques et leurs rapports mutuels*, were carried out with the view of settling definitely Prout's hypothesis; and no better idea can be obtained of how atomic weights are derived from, and compared with, a standard substance, than by considering very briefly some points of his work.

The first point to prove was clearly that a chemical compound, from whatever sources and however prepared, had the same composition; and, further, to determine the degree of accuracy to which this would hold. If pure chemical substances had not an absolutely identical composition, the atomic theory could hardly stand unless we assumed large and small atoms of the same kind, and then Prout's hypothesis might hold for some and not for others.

To test this, pure silver was prepared in various ways, and its purity tested by means of the same sample of sodium chloride, by determining the amount required to precipitate completely 10 grams of the silver. Silver distilled by the oxyhydrogen blow-pipe was found to be the purest, and was taken as the standard; several other processes, however, yielded it of a purity equal to 99.999 and 99.998 per cent.

The pure silver was now used to determine whether the amount of the chlorine in ammonium chloride prepared by totally different methods was constant. The ammonia required was prepared from (a) ammonium chloride purified from compound ammonias and other organic bodies, by boiling it with nitric acid; (b) from ammonium sulphate, heated to a high temperature with

strong sulphuric acid ; (c) by reducing potassium nitrite by means of zinc and potassium hydrate. In each case the ammonia was passed into pure water, and saturated with pure hydrochloric acid gas, evaporated down and sublimed in an atmosphere of ammonia at the atmospheric pressure. A fourth sample was sublimed *in vacuo*. Some of the determinations were carried out at ordinary temperatures, and some at 100° C.

Twelve determinations showed that 100·000 parts of silver, dissolved in nitric acid, required from 49·592 to 49·602 parts of ammonium chloride for complete precipitation.

The numbers are—

Series I.	Series II.	Series III.	Series IV.
49·600	49·598	49·5974	49·598
49·599	49·597	49·602	46·592
49·598	49·593	49·597	
	49·597		

It is quite apparent, then, that ammonium chloride, however prepared, has a composition absolutely constant within the limits of experimental error.

Again, it is not impossible, that although the proportions existing between the elements in a compound might be perfectly definite, yet they might not be exactly the same in another compound. If we take a series of potassium salts, as the chloride KCl, hypochlorite KClO, chlorite KClO₂, chlorate KClO₃, and perchlorate KClO₄, it is quite possible that careful investigation might reveal some modifying influence exerted by the oxygen on the relative proportions of the potassium and chlorine. To test this, Stas prepared in various ways silver chlorate, bromate, and iodate, and by means of

sulphurous acid reduced them completely to the state of chloride, bromide, and iodide, and proved that there was not a trace either of the halogen or of the silver in excess after the reduction. That is, then, that the ratio in which silver and iodine combine together to form the iodide is exactly the same for the iodate; and that the large amount of oxygen present in the latter compound has absolutely no effect on that ratio.

He concludes Part I. of the *Nouvelles Recherches* thus:—"Under the influence of sulphurous acid, the iodate, bromate, and chlorate of silver can then be brought to the condition of iodide, bromide, and chloride without any fraction, however small, of iodine, bromine, chlorine, or silver, becoming free. The uniform agreement of the results observed in the transformation of these three ternary compounds into the state of binary compounds demonstrates the invariability of the proportions by weight of the elements of which they are composed. I have likewise proved the constancy of composition of one of these binary bodies, in so far as this proof required to be given. It follows necessarily, from the combination of these two series of facts, that bodies unite in proportions which are absolutely fixed and invariable, that these proportions are real *constants*, and that the laws of chemical proportions which have served as the experimental basis of the atomic hypothesis are mathematical laws, as chemists have admitted them to be for more than half a century. The legitimate consequence which I am equally entitled to deduce from this is, then, that compounds produced under *the normal condition of their formation* ought necessarily to contain their *simple*

elements in the absolute proportions of these constants."

Having proved conclusively that the proportion of iodine to silver was exactly the same in both the iodide and the iodate, it was comparatively easy to determine the relative ratios of the atomic weights of silver, iodine, and oxygen.

To determine the composition of silver iodide was the first step, when it was found, by precipitating silver dissolved in nitric acid with hydriodic acid, that—

- I. 97.5915 grams of silver yielded 212.2905 of silver iodide.
 II. 43.5255 " " 93.6984 " "

whence from

Experiment I.	100.000	parts of silver yield	217.529	of the iodide.
II.	"	"	"	217.536 "
Mean,			217.5325	

By combining silver directly with iodine, he found that 96.7964 grams of iodine combined with 82.3601 of silver = 179.1565 of silver iodide, which, when collected, was found to weigh 179.1590 grams, whence 100.000 of silver gave 217.5300 of the iodide.

Having thus determined the composition of the iodide with great accuracy, the iodate was analysed completely. 98.275 grams were heated and left 81.5925 of the iodide, giving off 16.6825 of oxygen, which was collected by being passed over red-hot copper and weighed as oxide.

This gives a percentage composition of

Silver iodide,	83.024
Oxygen,	16.976

Assuming then that in the iodate there are three

36 RATIO OF SILVER IODIDE TO OXYGEN.

atoms of oxygen in a molecule of the iodate (which we infer from its analogy with the chlorine salts, &c.), we get the equivalent of the iodate by calculating how much of it contains $16 \times 3 = 48$ parts by weight of oxygen (taking 16 as the atomic weight of oxygen). This gives us

$$\begin{array}{rcl} 282.753 & \text{for } \text{AgIO}_3 & \\ 234.753 & \text{for } \text{AgI} < \begin{array}{l} 107.916 \text{ for Ag} \\ 126.837 \text{ for I} \end{array} & \\ 48 & \text{for } \text{O}_3 & \end{array}$$

The mean of a large number of experiments gave

$$\left. \begin{array}{l} 107.928 \text{ for the atomic weight of silver} \\ 126.857 \quad \quad \quad \text{iodine} \end{array} \right\} \text{when O} = 16.$$

Experiments carried out in the same way with the bromate gave

$$\begin{array}{rcl} 107.921 & \text{for the atomic weight of silver} & \\ 79.94 & \quad \quad \quad \text{bromine} & \end{array}$$

and with the chlorate

$$\begin{array}{rcl} 107.937 & \text{for the atomic weight of silver} & \\ 35.458 & \quad \quad \quad \text{chlorine.} & \end{array}$$

Now, the nitrate (AgNO_3) has a similar formula to that of the chlorate (AgClO_3), and if we can find the difference in their equivalents, we will obtain the difference between the atomic weight of chlorine and that of nitrogen; but we know that of chlorine, hence we get that of nitrogen. Further, by boiling a chloride such as that of potassium with nitric acid, with suitable precautions we can expel the whole of the chlorine and obtain the nitrate instead. Here we get then a gain due the difference between the

equivalents of the groups (NO_3) and (Cl), but to utilise this we must know the equivalent of the metal with which these groups are combined.

In determining the nitrate produced from a given weight of silver, Stas found 136.2952 grams of silver gave 214.6600 grams of the nitrate, or 100.000 of silver gave (as a mean of many determinations) 157.484 grams of the nitrate.

Taking the atomic weight of silver as 107.93, we get 169.972 as the molecular weight of the nitrate; that of the silver and the oxygen it contains is $107.93 + 48 = 155.93$, leaving for the atomic weight of nitrogen 14.042.

Knowing the atomic weights of the halogens, we readily determine the equivalents of the metals from their haloid salts. The bromides are the best for this purpose, because of the accuracy with which we may determine the exact equivalence to silver.

To determine, for example, the atomic weight of potassium, 25.1143 grams of pure potassium bromide were added to 22.792 grams of silver dissolved in nitric acid. After precipitation, .031 of silver remained in solution, whence it follows that 25.1143 grams of potassium bromide are equivalent to $(22.792 - .031) = 22.761$ of silver.

If $\text{Ag} = 107.93$, then

$$\text{KBr} = \frac{25.1143}{22.761} \times 107.93 = 119.088$$

$$\text{Br} = 79.955$$

$$\text{K} = 39.133$$

Similarly, for sodium, $\text{Na} = 23.04$

and lithium, $\text{Li} = 7.02$

Applying Penny's process, we find that we gain per equivalent for the change (as a mean)

KCl to KNO ₃ . . .	26·586
NaCl „ NaNO ₃ . . .	26·591
LiCl „ LiNO ₃ . . .	26·589
AgCl „ AgNO ₃ . . .	26·587

Mean value . . .	26·588
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Cl . . .	35·457
----------	--------

Equivalent of nitrate = metal +	62·045
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O ₃ . . .	48
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∴ Atomic weight of nitrogen = 14·045

Another element requiring special notice is carbon. Dumas and Stas in 1841 found that, in 5 experiments, a total weight of 5·398 grams of diamond, when burnt in oxygen, gave 19·789 grams of carbon dioxide,

Giving a ratio of C : CO₂ :: 5·398 : 19·789 = 1 : 3·666

For graphite they found in 9 experiments that 10·794 grams gave 39·588 grams of carbon dioxide, or C : CO₂ :: 1 : 3·668—

Whence for diamond C = 12·0032

„ graphite C = 11·9936

Erdmann and Marchand found with diamond C = 12·0032

„ „ graphite C = 12·0128 ;

Roscoe, with diamonds from the Cape of

Good Hope C = 12·00288

Stas checked these values by another ingenious and simple method, viz., passing carefully purified carbon monoxide over red-hot copper oxide, and weighing the dioxide produced as well as the loss of oxygen of the copper oxide.

In one experiment his absorption apparatus gained

31.935 grams, due to carbon dioxide; for the formation of this 11.6124 grams of oxygen were required.

$\therefore 31.935 - 11.6124 = 20.3226 =$ weight of carbon monoxide,

$11.6124 =$ „ oxygen in it,

$20.3226 - 11.6124 = 8.7102 =$ „ carbon in it,

as there is as much oxygen in the monoxide as was required to convert it into the dioxide; therefore

$$\text{O} : \text{C} :: 11.6124 : 8.7102 : 16 : x = 12.001.$$

We must next consider what is in many respects the most important ratio of all, but which, because of its great experimental difficulties, is far from being settled even now, in spite of the numerous researches on the subject. This is the ratio of the atomic weight of hydrogen to that of oxygen.

The two classical researches on this subject are those of Dumas and of Erdmann and Marchand, who determined the composition of water by passing pure hydrogen over copper oxide at a red heat, and collecting the water produced. Dumas in 19 experiments collected no less than 945.439 grams of water, for which he found 840.161 grams of oxygen were removed from the copper oxide, and hence the hydrogen was $945.439 - 840.161 = 105.278$, and hence

$$\text{H}_2 : \text{O} :: 105.278 : 840.161$$

and

$$\text{H} : \text{O} :: 1 : 15.96$$

His maximum value was 16.03, and his minimum 15.90. Erdmann and Marchand in 8 experiments found 429.352 grams of oxygen were required for 483.137 of water, and deduced exactly the same value, 15.96 for O. It is obvious that this process is very

liable to serious error, since any error is thrown on to the hydrogen, and then this relatively small number, being divided into the large one, a small error for the hydrogen becomes a large one in the oxygen value.

To obviate this, Cooke and Richards weighed the hydrogen in a large glass flask, which, being weighed first empty, then filled with hydrogen, the increase in weight gave the hydrogen which was converted into water by means of copper oxide. They found that in 16 experiments made in three series with hydrogen from different sources, that 6.7029 grams of hydrogen yielded 60.1687 grams of water. The values of the atomic weight of oxygen from the three series were respectively 15.952, 15.953, and 15.954. Lord Rayleigh pointed out, however, that he had detected an error in Regnault's method of weighing gases due to the shrinking of the glass vessels on exhaustion. The correction for this being applied, changed the value above found for the atomic weight of oxygen to 15.869 times that of hydrogen. Keiser weighed hydrogen occluded in palladium, from which it was expelled by heat and driven over copper oxide. He obtained 58.8626 grams of water from 6.5588 grams of hydrogen in 10 experiments, and deduces the value $H : O :: 1 : 15.949$.

If we know the ratio of the volumes in which the two gases combine, and likewise their relative densities, we may determine from these data the relative atomic weights.

Regnault determined the densities of hydrogen and oxygen with great accuracy, and by applying the correction shown by Lord Rayleigh to be necessary for shrinkage, Crafts finds the densities are (air = 1) .06949

for hydrogen and 1.10562 for oxygen, giving a relative density of 1 : 15.91.

Lord Rayleigh's determination of the relative density gave 15.884.

From the most recent experiments of the author, the ratio of the combining volumes is 2.0024 : 1, hence the value deduced from Regnault's experiments gives 15.89, and from Lord Rayleigh's 15.865.

It is evident, then, that as our most important and most exactly determined atomic weights are based on that of oxygen directly, that of hydrogen is eminently unfitted to be the unit, and that $\frac{1}{16}$ of that of oxygen has no disadvantage except a purely fanciful one. Further, so many of the elements may be represented as whole numbers, if we take $O = 16$, that calculations of all kinds will be much simplified, with no loss of accuracy.

A few examples are given below, which illustrate the chief methods adopted in determining atomic weights.

Aluminium.—Mallet found—I. From the ignition of ammonia alum, that it contained 11.2724 to 11.2793 per cent. of alumina.

II. From the ratio between aluminium bromide and the silver required to combine with the bromide, 100 parts of silver are equivalent to 82.455 of the bromide.

III. From the amount of hydrogen evolved in alkaline solution from the metal, 3.3520 grams of the metal gave 4161.6 c.cms. of gas = .37242 grams.

IV. From the conversion of the evolved hydrogen into water and weighing it, 10.3691 grams of aluminium gave 10.3515 grams of water.

Antimony.—Schneider reduced antimony trisulphide to antimony, and found that 28·52 per cent. of sulphur was contained in the sulphide.

Cooke reversed the process, and from antimony formed the trisulphide, and in this way obtained as his result that the sulphide contained 28·5182 per cent. of sulphur. Cooke also determined the amount of silver bromide formed by double decomposition between antimony tri-bromide and silver nitrate. 63·83 parts of antimony tri-bromide gave 100 parts of silver bromide. The iodide was similarly employed.

Boron.—Berzelius, and also Laurent, determined the atomic weight from the amount of water in crystallised borax, which contained as a mean 47·13 per cent. of water.

Calcium.—Dumas, as well as Erdmann and Marchand, employed the loss of weight which calcium carbonate undergoes on ignition, and which gives the ratio $\text{CaCO}_3 : \text{CaO}$, or $\text{CaCO}_3 : \text{CO}_2$. As a mean, 100 parts of calcium carbonate give 56·02 of lime.

Copper.—W. N. Shaw, by passing a galvanic current through two solutions, one of copper and the other of silver, from the amounts of the metals deposited, determined their relative atomic weights, $\frac{\text{Cu}}{2} : \text{Ag}$ being the ratio obtained.

Fluorine.—Although this element has only recently been obtained in the free state, its atomic weight has long been known and determined by one method, viz., the conversion of calcium fluoride into sulphate by means

of sulphuric acid, from which we get the ratio $\text{CaF}_2 : \text{CaSO}_4 :: 100 : 174.493$.

Magnesium.—The chief method adopted for this has been the conversion of the oxide into the sulphate. Dumas used his favourite process of double decomposition with silver nitrate, which in this case, as in so many, has proved unsatisfactory, from the difficulty of obtaining chloride free from oxide. Marignac used both the ratio $\text{MgO} : \text{MgSO}_4$ and the reverse $\text{MgSO}_4 : \text{MgO}$.

Manganese.—Hauer converted the sulphate into sulphide by heating in a current of hydrogen sulphide, when he got a very simple ratio $\text{MnSO}_4 : \text{MnS}$, which is practically $\text{MnSO}_4 : \text{O}_4$.

Dewar and Scott determined the ratio between silver permanganate and potassium bromide; and Marignac, at the same time, published results from the conversion of manganous oxide into manganous sulphate, which gave practically identical results.

Phosphorus.—Schrötter, by burning phosphorus to the pentoxide, found 100 grams of phosphorus gave 228.918 grams of pentoxide, whence we get the ratios $\text{P}_2 : \text{P}_2\text{O}_5$ and $\text{P}_2 : \text{O}_5$ at once. Dumas determined the ratio between the trichloride and silver, and found 42.455 grams of the chloride were equivalent to 100 grams of silver. These two very distinct methods agree extremely well.

In the following table it will be observed that the *non-metals* are distinguished by large capitals, the more *commonly* occurring metals in small capitals, and the *rarer* metals in ordinary type:—

Table of Atomic Weights, O = 16. (After OSTWALD.)

For use of different types in this table see preceding page.

ALUMINIUM, . Al = 27.1	Molybdenum, . Mo = 95.9
ANTIMONY	NICKEL, . . Ni = 59
(Stibium), . Sb = 120.3	Niobium, . . Nb = 94.2
ARSENIC, . As = 75.0	NITROGEN, . N = 14.041
BARIUM, . . Ba = 137.0	Osmium, . . Os = 192
Beryllium, . Be = 9.1	OXYGEN, . . O = 16.00
BISMUTH, . . Bi = 208.0	Palladium, . Pd = 106
BORON, . . B = 11.01	PHOSPHORUS, P = 31.03
BROMINE, . Br = 79.963	PLATINUM, . Pt = 194.8
Cadmium, . . Cd = 112.1	POTASSIUM,
Cæsium, . . Cs = 132.9	(Kalium), . K = 39.14
CALCIUM, . . Ca = 40.0	Rhodium, . . Rh = 103
CARBON, . . C = 12.0	Rubidium, . Rb = 85.4
Cerium, . . Ce = 140.2	Ruthenium, . Ru = 101.7
CHLORINE, . Cl = 35.453	Samarium, . Sm = 150
CHROMIUM, . Cr = 52.2	Scandium, . . Sc = 44.1
COBALT, . . Co = 59.0	SELENIUM, . Se = 79.1
COPPER (Cup-	SILICON, . . Si = 28.4
rum), . . Cu = 63.3	SILVER
Didy- { Neo-didy-	(Argentum), . Ag = 107.938
mium, { mium Nd = 140.8	SODIUM
mium, { Praseo-didy-	(Natrium), . Na = 23.06
mium, { mium, Pr = 143.6	STRONTIUM, . Sr = 87.5
Erbium, . . Er = 166.0	SULPHUR, . S = 32.06
FLUORINE, . F = 19.0	Tantalum, . . Ta = 183
Gallium, . . Ga = 69.9	TELLURIUM, . Te = 125
Germanium, . Ge = 72.3	Thallium, . . Tl = 204.1
GOLD (Aurum), Au = 197.2	Thorium, . . Th = 232.4
HYDROGEN, . H = 1.003	Thulium, . . Tu = 171
Indium, . . In = 113.7	TIN (Stannum), Sn = 118.1
IODINE, . . I = 126.86	Titanium, . . Ti = 48.1
Iridium, . . Ir = 193.2	Tungsten
IRON (Ferrum), Fe = 56.0	(Wolfram), . W = 184.0
Lanthanum, . La = 138.5	Uranium, . . U = 239.4
LEAD (Plumbum), Pb = 206.91	Vanadium, . V = 51.2
Lithium, . . Li = 7.03	Ytterbium, . Yb = 173.2
MAGNESIUM, . Mg = 24.38	Yttrium, . . Y = 88.7
MANGANESE, . Mn = 55.0	ZINC, . . . Zn = 65.5
MERCURY (Hy-	Zirconium, . Zr = 90.7
drargyrum), Hg = 200.4	

CHAPTER III.

ATOMIC AND MOLECULAR WEIGHTS.

IN the last chapter we gave the fundamental methods of determining molecular and equivalent weights, and from them the atomic weights of the elementary bodies. In this we propose to consider the chief subsidiary methods either for deciding definitely what multiple of the equivalent must be used when the methods previously given are inapplicable, or when they give results which are not conclusive. By far the most important method of checking the atomic weight is that to which we have very briefly referred, and what is known as Dulong and Petit's law. It may be written in its simplest form, "that the atoms of all the elements have the same capacity for heat;" or, putting it into a more directly practical form, we may write it "the atomic weight is inversely proportional to the specific heat," and bringing this to a numerical expression we have—

$$\text{The atomic weight of an element} = \frac{6 \text{ to } 6.6}{\text{Specific heat of the elements in the solid state.}}$$

This law was originally based on purely experimental evidence, and is, as a practical working law, only moderately accurate in its expression, and it cannot be otherwise, as we know that the specific heat of an element

varies with the temperature, but that the atomic weight is absolutely invariable. The following table shows the degree of accuracy to which the law holds for the majority of the elements in the solid state :—

	Atomic weight.	Specific heat.	Atomic weight × Specific heat.
Aluminium, . . .	27	·21	5·67
Antimony, . . .	120	·051	6·12
Arsenic, . . .	75	·081	6·07
Beryllium, . . .	9	·58	5·22
Bismuth, . . .	208	·031	6·45
Bromine, . . .	80	·084	6·72
Calcium, . . .	40	·17	6·8
Cerium, . . .	140	·045	6·3
Cobalt, . . .	59	·11	6·49
Copper, . . .	63	·094	5·92
Didymium, . . .	142	·046	6·53
Gallium, . . .	70	·079	5·53
Germanium, . . .	72	·077	5·54
Gold, . . .	197	·032	6·3
Indium, . . .	114	·057	6·5
Iodine, . . .	127	·054	6·86
Iridium, . . .	193	·033	6·37
Iron, . . .	56	·11	6·16
Lanthanum, . . .	138·5	·045	6·23
Lead, . . .	207	·031	6·42
Lithium, . . .	7	·941	6·59
Magnesium, . . .	24	·25	6·0
Manganese, . . .	55	·12	6·6
Mercury, . . .	200	·032	6·4
Molybdenum, . . .	96	·072	6·91
Nickel, . . .	59	·11	6·49
Osmium, . . .	192	·031	5·95
Palladium, . . .	106	·059	6·25
Phosphorus, . . .	31	·17	5·27
Platinum, . . .	195	·033	6·43
Potassium . . .	39	·17	6·63

	Atomic weight.	Specific heat.	Atomic weight × Specific heat.
Selenium, . . .	79	·075	5·92
Silver, . . .	108	·056	6·05
Sodium, . . .	23	·029	6·67
Sulphur, . . .	32	·16	5·12
Tellurium, . . .	125	·047	5·87
Thallium, . . .	204	·034	6·94
Tin, . . .	118	·056	6·61
Uranium, . . .	239	·028	6·69
Zinc, . . .	65	·094	6·11
Zirconium, . . .	91	·066	6·0

We see, then, from the above table the extent of the variation of the atomic heats of the elements as determined experimentally.

What we call the specific heat is, however, the sum of various thermal changes, which vary not only with the nature of the substance but with the range of temperature. The rate of expansion and the gradual change of state are amongst the causes of this variation. It is quite possible, then, that the law as we enunciated it at the beginning of the chapter may be absolutely accurate, although we are unable to prove that it is anything more than approximate.

One of the most interesting cases of variation is that of the three elements—carbon, boron, and silicon—of which the atomic heats deduced from the specific heats at ordinary temperatures give respectively the products :—

Carbon as diamond,	1·58
„ „ graphite,	1·93
Boron,	2·71
Silicon,	4·75

If the temperature, however, be a very high one, we have—

	Degrees.	Atomic heat.
Diamond,	at 985	5·51
Graphite,	,, 978	5·50
Boron,	,, 233	4·26
Silicon,	,, 232	5·68

showing that we may have these elements, which deviate so much from the law at ordinary temperatures, in perfect accord with it at elevated temperatures.

Another element, the atomic weight of which was for a long time in doubt, is beryllium, of which the oxide may be written BeO , $\text{Be} = 9\cdot1$, $\text{O} = 16$, or Be_2O_3 , where $\text{Be} = 13\cdot65$, $\text{O} = 16$. At ordinary temperatures its specific heat (Nilson and Pettersson) is $\cdot3973$, but at about 260° rises to $\cdot582$, hence $9\cdot1 \times \cdot582 = 5\cdot3$, but $13\cdot55 \times \cdot582 = 7\cdot9$, which is far too high. Hence $9\cdot1$ is adopted as the most probable value for the atomic weight of beryllium.

To take one other instance, that of uranium, the constitution of the oxides and salts of which are abnormal, hence conclusions drawn from their composition are far from decisive. The oxides which were formerly written UO and U_2O_3 , with an atomic weight of 120, are now UO_2 and UO_3 , and the atomic weight 240. Zimmermann found that the specific heat of uranium (fused) between 0° and $100^\circ \text{C.} = \cdot02765$.

$$\cdot02765 \times 240 = 6\cdot636 = \text{atomic heat.}$$

This, therefore, agrees with the number which had been adopted as the most probable.

A very important point at once suggests itself. Can we determine the molecular weight of a salt or other

compound from its specific heat? or, at least, can we detect any relation existing between them? The published works of Neumann in 1831, and Regnault in 1840, clearly proved that the connection between the molecular weight and the specific heat is a simple one, and that we may state the law connecting them thus:—
The specific heat of the elements is practically the same whether they are in the free state or in combination. It is evident, then, that we may deduce the specific heat of many elements in the solid state which we cannot determine directly, such as those of hydrogen, oxygen, and nitrogen. Regnault deduced the specific heats of the alkali metals from those of their haloid salts, and found the results agreed very well with his direct observations afterwards, showing that they obeyed Dulong and Petit's law:—

KCl=74.5	Sp. ht. = .173
$74.5 \times .173 = 12.44 = \text{molecular heat} = 2 \times 6.22$	
NaCl=58.5	Sp. ht. = .214
$58.5 \times .214 = 12.52 = \text{molecular heat} = 2 \times 6.26$	
KBr=119	Sp. ht. = .113
$119 \times .113 = 13.45 = \text{molecular heat} = 2 \times 6.72$	
NaBr=103	Sp. ht. = .137
$103 \times .137 = 14.1 = \text{molecular heat} = 2 \times 7.0$	
KI=166	Sp. ht. = .0819
$166 \times .0819 = 13.59 = \text{molecular heat} = 2 \times 6.79$	
NaI=150	Sp. ht. = .0881
$150 \times .0881 = 13.215 = \text{molecular heat} = 2 \times 6.6$	

The above determinations show that it is highly probable that chlorine obeys Dulong and Petit's law as we know iodine and bromine do, from direct experiment.

If we take another case—the chlorides and iodides of mercury :—

Mercuric chloride, $\text{HgCl}_2 = 271$, sp. ht. = $\cdot 069$ $271 \times \cdot 069 = 18\cdot 7 = 3 \times 6\cdot 23$	Mercurous chloride, $\text{Hg}_2\text{Cl}_2 = 471$, sp. ht. = $\cdot 052$ $471 \times \cdot 052 = 24\cdot 5 = 4 \times 6\cdot 12$
Mercuric iodide, $\text{HgI}_2 = 454$, sp. ht. = $\cdot 042$ $454 \times \cdot 042 = 19\cdot 07 = 3 \times 6\cdot 36$	Mercurous iodide, $\text{Hg}_2\text{I}_2 = 654$, sp. ht. = $\cdot 0395$ $654 \times \cdot 0395 = 25\cdot 83 = 4 \times 6\cdot 46$

At first sight it might seem that this settled the formulæ for the mercurous salts, as it seems a natural consequence of the law that the mercurous salts, having a lower specific heat than the mercuric salts, ought to have a higher molecular weight. This by no means follows, for if we try the formula HgCl for mercurous chloride, we have taken half the molecular weight and half the number of atoms, as

$$\begin{aligned} \text{HgCl} &= 235\cdot 5 & \text{Sp. ht.} &= \cdot 052 \\ 235\cdot 5 \times \cdot 052 &= 12\cdot 25 = 2 \times 6\cdot 12 \end{aligned}$$

which is the same result as above.

From this it is apparent that we are unable to deduce the molecular weight of a salt, but that does not prevent our deriving valuable information regarding it. We might use it to determine whether fluorine was more like oxygen than chlorine, and the formula of fluorspar,

$$\left. \begin{array}{l} \text{CaF like CaO (F=38)} \\ \text{or CaF}_2 \text{ like CaCl}_2 \end{array} \right\} \text{The specific heat is } \cdot 2154$$

$$78 \times \cdot 2154 = 16\cdot 8 = \text{either } 2 \times 8\cdot 4 \text{ or } 3 \times 5\cdot 6$$

whence three atoms are more probable, and more so if we take away $6\cdot 8$, the known atomic heat of calcium, which leaves $10\cdot 0$ as the remainder for the atomic heat of one or of two atoms of fluorine, of which the atomic

heat is far more likely to be under than over 6; hence we find 5.0 as its atomic heat from this compound. We may find that of oxygen from potassium chlorate and perchlorate:—

KCl	= 74.5	Sp. ht. = .173	∴ Molecular heat =	12.4
KClO ₃	= 122.5	,, = .209	∴ „ =	25.6
KClO ₄	= 138.5	,, = .19	∴ „ =	26.3
		25.6 - 12.4 = 13.2	for O ₃	
		26.3 - 12.4 = 13.9	,, O ₄	
		27.1	,, O ₇ ∴ 3.9 for O	

Now, if we take the compounds of carbon, boron, and silicon, we find that their atomic heats, deduced from those of their compounds, as from direct experiments, have an abnormally low value.

K ₂ CO ₃	= 138	Sp. ht. = .206	∴ Mol. ht. =	28.4
K ₂	= 2 × 6.5 = 13.0	O ₃	= 3 × 3.9 = 11.7	
∴ At. ht. of C	= 28.4 - (13.0 + 11.7)			= 3.7

Lead carbonate, PbCO₃, gives similar results.

PbCO ₃	= 267	Sp. ht. = .079	Mol. ht. =	21.1
Pb	= 6.5 and O ₃	= 11.7	∴ At. ht. of C	= 21.1 - (11.7 + 6.5) = 2.9

The specific heats of their compounds increase rapidly with the temperature, as beeswax, of which the specific heat is from—

—21°	to	3° C.	=	.4287
6°	,,	26° C.	=	.504
26°	,,	42° C.	=	.82
42°	,,	58° C.	=	1.72

carbon trichloride, C₂Cl₆—

18°	to	37° C.	=	.178
18°	,,	43° C.	=	.194
18°	,,	50° C.	=	.277

If we assume the atomic heat of chlorine constant at 6·4, from these three numbers we get the molecular heat respectively 42·2, 46·0, and 65·6, whence the atomic heat of carbon is 1·9, 3·8, and 13·6. This shows the influence of the temperature in a very marked manner, and that some limiting clause is absolutely essential before the law can be utilised for giving the atomic heat with accuracy.

The specific heat in the liquid state of the few elements is in every case for which it is known, a little higher than of the same elements in the solid condition.

In the gaseous condition we have greater difficulty in framing a law which will express a definite relation between the composition and specific heat. In the case of solids, the external work (such as expansion) done is small, and what we have most difficulty in allowing for is change of state and molecular condition, which not only in themselves absorb or give out heat, but the different modifications have themselves different specific heats. If we take phosphorus as an example, we see Kopp's value for yellow phosphorus is (13° to 36°) ·202, and Regnault's for red (15° to 98°) ·1698, and for selenium (Rettendorf and Wüllner), we have the crystallised modification having a specific heat of ·084, and the amorphous ·112, through the same range of temperature. In gases, however, we have much external work, and also more internal motion in the individual molecule than is possible for it in the solid state. The external work done by a gas in expanding can readily be estimated from the mechanical theory of heat. We find that the ratio of the specific heat at *constant volume*—that is, where the gas is not allowed to expand—to

that at *constant pressure*—that is, where it is allowed to do so—is not constant, those gases which have a very simple molecule giving a much higher ratio than those of which the molecule is more complex, and in which the ratio of the internal work to the external is much greater, as the following examples show :—

	Sp. ht. at const. vol.	Sp. ht. at const. press.	Atoms in molecule.
Mercury,	1	1·66	1
Hydrogen,	1	1·38	2
Air,	1	1·40	2
Hydrochloric acid, at 20°, .	1	1·40	2
„ „ at 100°, .	1	1·39	2
Carbon monoxide,	1	1·40	2
Carbon dioxide, at 0°, .	1	1·31	3
„ „ at 100°, .	1	1·28	3
Ethylene, at 0°,	1	1·24	6
„ at 100°,	1	1·187	6

We see, then, that more heat proportionately is required for the 6-atomed molecule of ethylene than for that of carbon dioxide, and that it requires more than the gases of which the molecule contains two atoms, and that those given are all alike, the ratio being 1 : 1·4, while for mercury the ratio is still larger, or the internal work done much smaller. This confirms in a most interesting manner the correctness of our views as to the mon-atomic nature of the mercury molecule.

Chlorine, a coloured gas, behaves differently from the other gases with similarly constituted molecules, for the ratio of its two specific heats is as 1 : 1·323, and for bromine and iodine 1 : 1·294.

Another method which has at various times proved of considerable utility, and is of great interest, is that compounds of analogous composition very often crystallise

in exactly the same crystalline forms, and we in this way can deduce the necessary formulæ, and hence the atomic weights of the component elements. Substances crystallising in the same form are said to be *isomorphous*. An extremely good example is afforded by the common substances known as alums, aluminium sulphate and potassium sulphate crystallise along with water and give what is called potash alum, a double sulphate of aluminium and of potassium; and the alums in general are double sulphates, one of which corresponds to that of aluminium, the other to that of potassium. Alums can be formed from the following sulphates, each consisting of one from each class + $24\text{H}_2\text{O}$:—

Aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$	Potassium sulphate, K_2SO_4
Ferric ,, $\text{Fe}_2(\text{SO}_4)_3$	Sodium ,, Na_2SO_4
Chromic ,, $\text{Cr}_2(\text{SO}_4)_3$	Ammonium ,, $(\text{NH}_4)_2\text{SO}_4$
Manganic ,, $\text{Mn}_2(\text{SO}_4)_3$	Silver ,, Ag_2SO_4
	Thallium ,, Tl_2SO_4

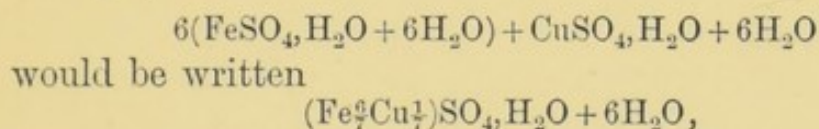
From this we see that aluminium salts correspond to the ferric salts, and hence Al_2O_3 was chosen as the formula for alumina to correspond to Fe_2O_3 , and not AlO to correspond to FeO and ZnO . Again, the silver and thallium alums are very interesting corroborations of the formulæ assigned to the salts of these metals.

From isomorphism we get some insight into the constitution of several compounds. The spinelle group has the general formula M_3O_4 , or it may be $\text{MO}, \text{N}_2\text{O}_3$, that is, we may have two metals, or only one, combined with oxygen, as

Fe_3O_4 , or $\text{FeO}, \text{Fe}_2\text{O}_3$	Magnetic iron oxide.
$\text{FeO}, \text{Cr}_2\text{O}_3$	Chrome iron ore.
$\text{MgO}, \text{Al}_2\text{O}_3$	Spinelle.

The vitriol group of sulphates, having the general

formula $\text{MSO}_4, \text{H}_2\text{O} + 6\text{H}_2\text{O}$, of which $\text{MgSO}_4, \text{H}_2\text{O} + 6\text{H}_2\text{O}$ may be taken as the type, contains the ferrous, cupric, zinc, nickel, cobalt, and manganous sulphates. Although when alone, and under ordinary conditions, these may not always crystallise in the typical form, yet on crystallising a mixed solution, all will crystallise together, and it will be impossible to separate a mixture of these sulphates by any amount of recrystallisation. Ordinary copper sulphate crystals consist of $\text{CuSO}_4, \text{H}_2\text{O} + 4\text{H}_2\text{O}$, but if a certain amount of ferrous sulphate be added, and the solution be strong enough to crystallise, and the crystallisation be started with a crystal of ordinary ferrous sulphate, every crystal will contain both iron and copper, and for every SO_4 there will be $7\text{H}_2\text{O}$, so the formula is often written $(\text{CuFe})\text{SO}_4, \text{H}_2\text{O} + 6\text{H}_2\text{O}$. The amount of the metal equivalent to the sulphuric acid being in part iron and in part copper, the formula expresses the analytical results, rather than a true molecule, and (to take an example) what ought to be represented as

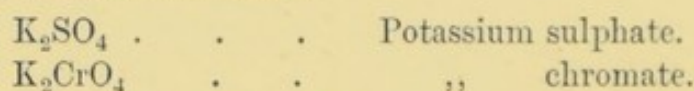


the true meaning being really that $56 \times \frac{6}{7}$ of iron + $63 \times \frac{1}{7}$ of copper = 48 parts of iron + 9 parts of copper are united with 96 parts of sulphion (SO_4) and 126 parts of water. 48 parts of iron require $96 \times \frac{6}{7}$ of the $\text{SO}_4 = 82\frac{2}{7}$, whilst the 9 parts of copper require $96 \times \frac{1}{7} = 13\frac{5}{7}$ parts.

An interesting point about this group is the difference in relationship of one molecule of the water from the other six molecules to the central group of the crystallised salt. Dried at 100°C ., or even many degrees

higher, only six molecules of water are expelled. A very much higher temperature is required to drive off the last molecule. If we add to a solution of ferrous sulphate, for example, an equivalent quantity of ammonium sulphate, we get crystals of ferrous ammonium sulphate, of which the formula is $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O}$, crystallising in exactly the same form, but all the water is driven off at 110°C . The ammonium sulphate, therefore, seems to occupy the same position in the salt that the last molecule of water held. This salt is much used in analysis, as it contains exactly $\frac{1}{7}$ of its weight of metallic iron in the *ferrous* condition, and must not be confounded with iron ammonium alum, $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O}$, which has the iron in the *ferric* condition.

Chromates and sulphates crystallise in the same form, and have similar formulæ—



These two salts crystallise together, and the proportion of chromium and sulphur in crystals obtained from a mixed solution depends on the relative proportions of each salt in the solution. Hence potassium chromate is often adulterated with the much cheaper sulphate, the high tinctorial power of the chromate rendering even a large amount of sulphate undetectable from the colour. The lead and barium salts are also both extremely insoluble, so that the ordinary tests for sulphuric acid are precluded. If, however, we remove the oxygen from the chromate, and reduce 2CrO_3 to Cr_2O_3 by boiling the chromate with hydrochloric acid and alcohol, we may then apply the barium chloride test

for sulphuric acid, as it is the CrO_3 and the SO_3 groups that are alike.

Very often groups which we do not usually think of as similar seem to give rise to isomorphous salts. One of the most interesting cases is that of carbonates of certain diad metals and nitrates of monad metals. Calcium carbonate crystallises in two perfectly distinct forms—calcspar and arragonite—of which the densities are respectively 2.71 and 2.94. The crystalline form of calcspar is almost the same as that of sodium nitrate, and by placing a crystal of calcspar in a solution of sodium nitrate it will grow by the deposition of sodium nitrate all over it in the same way that the very dark crystals of chrome alum may be covered by colourless aluminium alum. Arragonite has the same crystalline form as potassium nitrate, so we have

Calcspar,	CaCO_3
Sodium nitrate,	NaNO_3
Arragonite,	CaCO_3
Potassium nitrate,	KNO_3

Isomorphous bodies, in the strictest sense, are generally defined as those not only which crystallise in the same forms, but which are capable of replacing one another in any proportions in these forms.

Another method, of however but little importance, with regard to the atomic weights of the elements or the molecular weights of inorganic compounds is the atomic volume. As the product of volume by density gives the mass, if we divide the molecular weight by the density, we get the volume corresponding, which is known as the molecular volume. Of the great importance of this, especially with regard to organic com-

pounds, we shall afterwards treat at greater length ; at present we shall only point out that many groups of similarly constituted bodies have nearly the same atomic volumes.

	Molecular weight.	Density.
Calcium sulphate, CaSO_4 . . .	136	$\div 3\cdot0 = 45\cdot3$
Strontium sulphate, SrSO_4 . . .	183	$\div 3\cdot9 = 47\cdot0$
Barium sulphate, BaSO_4 . . .	233	$\div 4\cdot5 = 51\cdot4$

Science is indebted to Raoult of Grenoble for two processes of determining the molecular weights of substances in the liquid state which are of great interest and value, because of the power they give of attacking many problems from an altogether different standpoint. Everyone knows that sea water does not freeze nearly so readily as pure water. It is likewise well known that the ice formed from the sea in cold climates is almost free from salt.

Raoult states, as a general law, that *every substance in dissolving in a definite liquid capable of solidifying, lowers the solidifying (or freezing) point of the liquid*, and that there are no exceptions to this law. It follows that if we have two samples of a substance, the purer is that which solidifies at the higher temperature. When a dilute solution is cooled, the first portions which solidify consist of the solvent almost in a state of purity, and that as the liquid becomes in this manner more and more concentrated the solidifying point falls lower and lower. This gives a further test of the purity of a substance, for if the temperature at which it solidifies remains the same from the beginning till all is solid, then it must be pure, as in the case of glacial acetic acid, the strongest freezes at 17°C. , but if a very small quantity of water be

added it will not freeze till its temperature falls to 10°C. ; similarly carbolic acid (phenol), unless quite anhydrous, tends to remain liquid at ordinary temperatures.

The temperature at which solidification *commences* alone is fixed, and this is called *the solidifying point*, and the fall of the solidifying point is the difference between that of the solution and of the solvent determined within a few hours of each other. About 100 cubic centimetres should be used, and the temperatures read to $\frac{1}{20}$ of a degree Centigrade at least, for determining molecular weights. The *coefficient of fall* is the quotient of the fall of temperature in the freezing point by the weight of the substance in 100 grams of the solvent.

The *molecular fall* is obtained by multiplying the coefficients of fall by the molecular weight (the solution to be dilute).

It is then found that the molecular falls, produced by the various compounds which can be dissolved in the same solvent, are all grouped under a small number of constants.

If water be employed as the solvent, the molecular fall is very nearly the same, and very close to 19 for all organic compounds except the amines. It is also 19 for feeble mineral acids and bases, as hydrosulphuric and sulphurous acids, and for ammonia. It is about 35 for all alkaline salts of monobasic acids, for alkalis and strong monobasic acids, as potassium chloride, nitrate, and hydrate. It is nearly 40 for neutral alkaline salts of the dibasic acids, and these acids themselves, as potassium sulphate and chromate, and for sulphuric acid. It is nearly 45 for the alkaline earths, and their

salts with monobasic acids, as barium hydrate, chloride, and nitrate.

If we use acetic acid instead of water, it is in almost every case 39, except in the cases of sulphuric and hydrochloric acids, and of magnesium acetate, for which three it is only 19—that is to say, the half of that of other substances.

By using benzene as the solvent, we get two groups, the molecular fall for acids and alcohols 25, and for other organic substances and the chlorides of the non-metals 49. The law may be generally stated that “if the molecular weight of any substance whatever be dissolved in 100 times the molecular weight of any organic solvent, and the fall of the freezing point determined, it will be found to be about $\cdot 62^{\circ}$ C; if it be exceptional, it will be almost exactly $\cdot 31^{\circ}$ C.” To determine the molecular weight, then, we have

$$\text{M.W.} = 39 \times \frac{100 \times q}{cp} \text{ for acetic acid.}$$

Where q = quantity of substance studied.

p = quantity of solvent.

c = fall of point of solidification.

One has only to replace the 39 by the numbers given above to adapt it for the other solvents.

Another well-known fact is that the tension of water from solutions of salts is not as great as from pure water, or, to put it in another way, the boiling point is higher for salt water than for pure water, a fact made use of in the laboratory for keeping bodies at a few degrees over 100° , by using baths of solutions of calcium and zinc chlorides, &c. By measuring the tension of the pure solvent f , and that of the solution f' , and

dividing the difference by the tension of the solvent, we get what Raoult calls the relative difference of tension of vapour $= \frac{f-f'}{f}$. This relative difference of the tension is independent of the temperature (at least when the tension of the solvent is from 400 to 760 mm.). It, however, varies with the concentration of the solution, but for solutions containing less than 7 molecules of the dissolved matter for 100 of the solvent, the variation of the relative difference of tension follows a law similar to that of the fall of the freezing point. When the solutions contain more than 10 molecules of the solid for 100 of the solvent, the relative difference of the tension diminishes in an indefinite manner as the concentration is increased.

It is therefore possible to calculate the "molecular diminution of tension," produced by a molecular weight in grams dissolved in 100 grams of the solvent by means of the following formula:—

$$\frac{f-f'}{fw} \times \text{M. Wt.}$$

where w = weight of solid, dissolved in 100 grams of solvent.

As in the case of the solidifying point, we find these "molecular diminutions of tension" arranging themselves into a small number of groups. If the molecular diminution of tension, as obtained above, be divided by the molecular weight of the liquid, the quotient obtained will represent the relative diminution produced by 1 molecule of the solid dissolved in 100 of the volatile solvent. This number seems to be

a constant, having in almost all cases a value of $\cdot 0105$.

In other words, 1 molecule of non-volatile substance dissolved in 100 molecules of any volatile liquid whatever diminishes the tension of its vapour by a constant fraction of its value, and this fraction is equal to $\cdot 0105$ of its amount.

Li. Na. K
 S. Se. Te.
 Ca. Sr. Ba.
 Fe. Co. Ni.

CHAPTER IV.

CLASSIFICATION OF THE ELEMENTS.

HAVING briefly considered the various modes of determining the atomic weights of the elements, in which use has been made of various relationships which have been discovered to exist between the molecular weights and the physical properties of chemical substances, we have now to consider the elements more directly with regard to one another. In chemistry, as in other branches of science, there have been many systems of classification in use at various times, some very artificial, depending on one property alone of the classified substances as their basis, others more or less natural, taking into account several properties at the same time.

The elements are often divided into two classes known as *metals* and *non-metals*, sometimes called *metalloids*. The metals were defined as elements possessing metallic lustre, and being fair conductors of heat and electricity. It was hardly to be expected that such a classification, depending on purely physical properties, would be very satisfactory for chemical purposes, and such was found to be the case. Attempts to classify the elements on a chemical basis, such as their behaviour towards certain other substances, met with perhaps greater success; but in all there was a residue of elements which were unlike one another, and yet not so much so as to be worthy of

each having a class for itself. One excellent manual of chemistry adopts a classification of which the ninth class is "*Copper, Lead, and Thallium, metals which are not closely related.*"

The arrangement of the elements in an electro-chemical series was one of the simplest arrangements of the whole of the elements in one series, which brought many of the similar metals together and roughly divided them into groups. The element considered usually to be most electro-negative is oxygen, and the following table, in which the most electro-positive elements come last, is given in Jenkin's *Electricity and Magnetism*:—Oxygen, sulphur, nitrogen, fluorine, chlorine, bromine, iodine, phosphorus, arsenic, boron, carbon, antimony, silicon, hydrogen, gold, platinum, mercury, silver, copper, bismuth, tin, lead, cobalt, nickel, iron, zinc, manganese, aluminium, magnesium, calcium, barium, lithium, sodium, potassium. We can only call it *an* electro-chemical series, however, and we may determine the position of many elements in such a series by placing them two at a time in one liquid, but not in contact, connecting them with a wire, and observing the direction of the current through it. If we use different liquids with the same two elements we will find for many pairs the current now flows in one direction and now in the opposite. We may also test by replacing one element in a compound by another. If we place zinc in dilute sulphuric acid the zinc turns out the hydrogen, therefore hydrogen is less electro-positive than zinc; cadmium also will turn hydrogen out, and zinc in turn will replace it, so we arrange these three—hydrogen, cadmium, zinc.

Thenard's classification of the metals was based on the

temperature at which they decomposed water. It is somewhat as follows :—

- I. Metals decomposing water at ordinary temperature, as *potassium, sodium, lithium*, producing alkalies, and *barium, strontium, and calcium*, producing alkaline earths.
- II. Metals decomposing water at 100° C.—*magnesium and aluminium*.
- III. Metals decomposing water at a red heat.
 - (a) Those which also give off hydrogen in presence of cold dilute acids—*manganese, zinc, iron, nickel, cobalt, cadmium, chromium*.
 - (b) Those which give off hydrogen in presence of boiling alkalies—*tin, antimony*.
- IV. Metals decomposing water at a white heat, but giving off no hydrogen when treated with cold acids—*copper, lead, bismuth*.

The oxides of the metals of all the above groups are not decomposed by heat into metal and oxygen.

- V. Metals which do not decompose water at any temperature, and of which the oxides when heated are resolved into oxygen and metal (noble metals)—*mercury, silver, gold, platinum*.

This is not a satisfactory classification in many ways. Manganese most probably should be relegated to Class II., and the real position of aluminium is doubtful. Traces of impurity make great differences in such reactions. Pure zinc placed in pure dilute sulphuric acid gives off no hydrogen, but if a drop of a solution of a lead or copper salt be added, action begins vigorously from galvanic action thus set up between the zinc and

the lead or copper deposited. Another classification which has many points of advantage is that based on the *atomicity* of the element, that is, on the number of atoms of hydrogen which can combine with or replace one atom of the element. We will not go into this in any further detail, but consider one classification, which, if not based directly on atomicity or valency, at any rate brings it out as a prominent feature.

There are many groups of the elements which form well-defined families, each member differing in a more or less definite way from its companions, for example, the chlorine family, where, if we arrange the members in the order of their atomic weights—that is, fluorine, chlorine, bromine, and iodine—we have, as far as hydrogen and the metals are concerned, far greater chemical activity displayed the lower the atomic weight, but just the reverse with regard to oxygen, for iodine pentoxide is a stable body, but all the oxides of chlorine are eminently unstable and readily decompose into their elements with explosive violence, and at present no oxygen compounds of fluorine are known. It is only recently that hydrofluoric acid has been satisfactorily decomposed and the fluorine separated from the hydrogen. Iodine, on the other hand, forms the unstable and, under certain circumstances, explosive, hydriodic acid.

Taking electro-positive elements, we have lithium, sodium, potassium, rubidium, and caesium. Again, as the atomic weight increases, we have a definite increase in the tendency to form compounds with oxygen, which are more and more difficult to decompose, caesium only having been obtained quite recently in the free state because

of the very great difficulty of separating it from the negative elements with which it was combined.

There seems, then, to be a certain connection between the atomic weight and the chemical behaviour of the members of families of the elements whether we look at the non-metals or at the metals.

Newlands, in 1864, pointed out that if we arrange the elements in the order of their atomic weights we have them breaking naturally into groups of seven, in which the first member of each set is of a similar nature, and in the same way with the second, third, and so on. Newlands expressed this periodic recurrence of the properties of the elements thus arranged in what he termed the law of octaves, so called because each eighth and fifteenth element, starting from any element as the first, seemed to be related to one another in much the same way as a note in music to its octaves.

This mode of classification has been carried out and elaborated in much greater detail by Mendelejeff, Lothar Meyer, and others.

The *Periodic Law* may be briefly stated thus:—The properties of the elementary substances vary in a periodic manner with their atomic weights.

If we arrange all the elements at present known we find not only a few gaps, but also in several cases groups of three or four elements of almost identical atomic weight, and very similar properties, as cobalt, nickel, iron, and manganese. These seem to tend to recur at the end of each second series, and Mendelejeff calls the series alternately large and small periods, as we see in the following table, which gives his arrangement of the elements, along with their densities and

atomic volumes. The plate shows Lothar Meyer's curve of the atomic volumes. The melting points and other physical constants show a periodic variation similar to that of the atomic volumes.

Looking briefly at the various series as they are presented to us in the table, we have first of all the isolated hydrogen, the other members of its period being at present entirely unknown. Its reactions indicate a metallic nature, and it may be regarded as the vapour of a very volatile metal.

The other members of the series seem to set into two groups, those of the small periods forming one group, and those of the larger periods forming the other.

In some of their compounds at least all act as monads. Copper, although a dyad in ordinary copper sulphate and oxide, forms several very stable compounds in which it may be compared to silver, as cuprous sulphide, Cu_2S , cuprous iodide, Cu_2I_2 , cuprous oxide, Cu_2O . Gold behaves also as a monad in aurous chloride, AuCl , though its commoner compounds are of the type of auric chloride, AuCl_3 and KAuCl_4 .

Silver, although in many ways very unlike the alkali metals, is undoubtedly a monad, as we see from its forming an alum, silver sulphate taking the place of the potassium sulphate in ordinary alum. This alone is not sufficient to place it in this group, for we must remember that thallium also forms an alum. Silver oxide is a powerful base, and completely neutralises the strongest acids. Sodium is the other metal which is in the small periods; and, although it differs in many ways from potassium, it is so unlike silver,

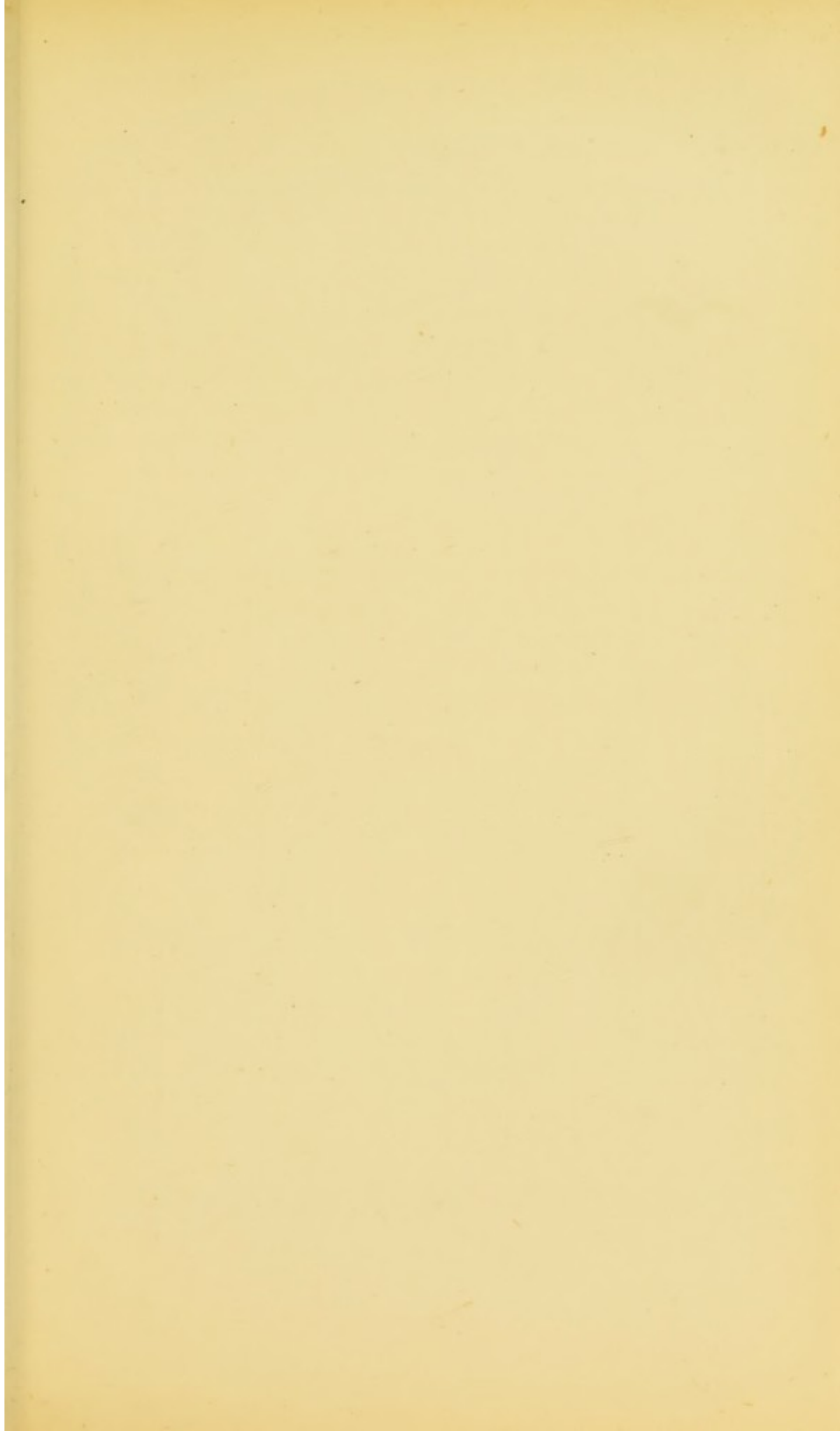
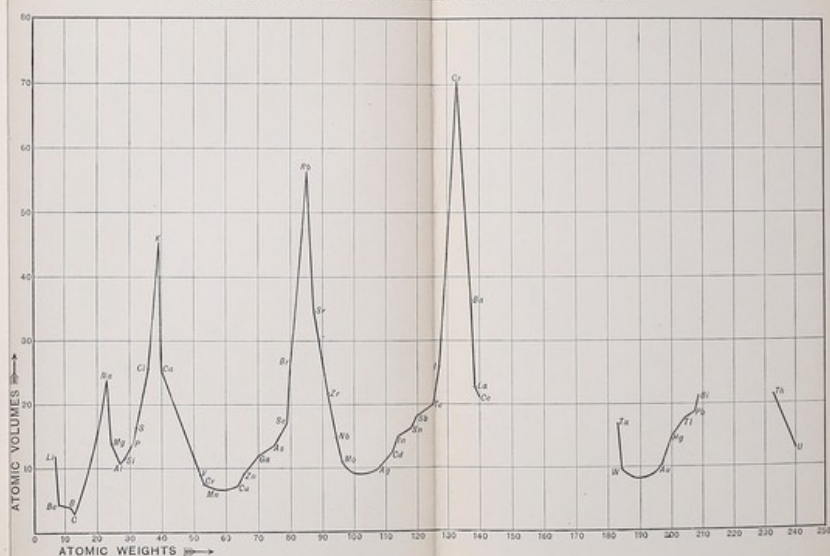


TABLE OF ATOMIC WEIGHTS, DENSITIES, AND ATOMIC VOLUMES.

Atomic Weight, Typical Compound,	I. NaCl	II. BeCl ₂	III. BCl ₃	IV. CCl ₄	V. or III. NH ₄ Cl NH ₃	VI. or II. SO ₂ H ₂ O	VII. or I. Cl ₂ O ₇ HF		
Atomic Weight,	Hydrogen, 1.008	—	—	—	—	—	—	—	—
Atomic Weight,	Lithium, 7.00	Beryllium, 9.1	Boron, 11.01	Carbon, 12.00	Nitrogen, 14.04	Oxygen, 16.00	Fluorine, 19.00	—	—
Density,	—	1.85	2.48	3.3	—	—	—	—	—
Atomic Volume,	11.9	4.9	4.1	3.6	—	—	—	—	—
Atomic Weight,	Sodium, 23.00	Magnesium, 24.36	Aluminium, 27.1	Silicon, 28.4	Phosphorus, 31.00	Sulphur, 32.06	Chlorine, 35.45	—	—
Density,	—	1.74	2.49	2.56	2.3	2.04	1.58	—	—
Atomic Volume,	23.7	14.0	10.7	11.2	15.5	15.7	25.7	—	—
Atomic Weight,	Potassium, 39.10	Calcium, 40.0	Scandium, 44.1	Titanium, 48.1	Vanadium, 51.2	Chromium, 52.0	Manganese, 55.00	Iron, 56.0	Cobalt, 59
Density,	—	1.57	—	—	5.5	6.5	8.0	7.9	8.5
Atomic Volume,	45.4	25.4	—	—	9.3	7.7	6.9	7.2	6.7
Atomic Weight,	Copper, 63.5	Zinc, 65.2	Gallium, 69.9	Germanium, 72.3	Arsenic, 75.0	Selenium, 79.1	Bromine, 79.96	—	—
Density,	8.8	7.15	5.96	5.47	5.62	4.6	2.77	—	—
Atomic Volume,	7.2	9.1	11.7	13.2	13.2	17.2	26.9	—	—
Atomic Weight,	Rubidium, 85.4	Strontium, 87.5	Yttrium, 89.7	Zirconium, 90.7	Niobium, 94.2	Molybdenum, 95.9	Ruthenium, 101.7	Rhodium, 103	Palladium, 106
Density,	1.52	2.5	—	6.15	7.06	8.6	12.25	12.1	11.5
Atomic Volume,	56.1	35.0	—	21.7	13.5	11.1	8.2	8.5	9.2
Atomic Weight,	Silver, 107.94	Cadmium, 112.4	Indium, 114.7	Tin, 118.7	Antimony, 120.3	Tellurium, 127.6	Iodine, 126.9	—	—
Density,	10.5	8.65	7.42	7.29	6.7	6.25	4.95	—	—
Atomic Volume,	10.5	12.9	15.2	16.1	18.0	20.0	25.6	—	—
Atomic Weight,	Cesium, 132.9	Barium, 137.3	Lanthanum, 138.5	Cerium, 140.2	—	—	—	—	—
Density,	1.93	3.51	6.1	6.7	—	—	—	—	—
Atomic Volume,	70.6	36.5	22.7	20.9	—	—	—	—	—
Atomic Weight,	—	—	Erbium, 166	Tantalum, 182	Tungsten, 184.0	—	Osmium, 192	Iridium, 193.2	Platinum, 194.8
Density,	—	—	—	16.8	19.11	—	22.48	22.42	21.5
Atomic Volume,	—	—	—	17.9	9.6	—	8.5	8.6	9.1
Atomic Weight,	Gold, 197.2	Mercury, 200.4	Thallium, 204.1	Lead, 208.0	Bismuth, 209.0	—	—	—	—
Density,	19.3	14.19	11.85	11.35	9.82	—	—	—	—
Atomic Volume,	10.2	14.1	17.2	19.2	21.1	—	—	—	—
Atomic Weight,	—	—	—	Thorium, 232.1	—	Uranium, 238.4	—	—	—
Density,	—	—	—	11.9	—	18.93	—	—	—
Atomic Volume,	—	—	—	19.1	—	12.9	—	—	—

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CURVE SHOWING VARIATION OF ATOMIC VOLUME WITH ATOMIC WEIGHT.



copper, and gold, and so much more like the remaining metals, that it is a serious impediment in the way of adopting the double period as a natural arrangement.

Lithium is in many points even more unlike the remaining elements of the group, as it forms no alum, and has an almost insoluble carbonate and phosphate; the carbonate is much more soluble in carbonic acid than in pure water, and is reprecipitated on boiling, hence it much more resembles a member of the calcium than of the potassium group. Potassium, rubidium, and cæsium resemble each other so much in almost all points, that it is very difficult to separate them from one another. They form a very well-defined family, with their properties varying with their atomic weights.

The second series, of which there are again two sets alternating with one another, have their oxides of the general formula MO , and are typical dyads. The two sets are—beryllium, calcium, strontium, and barium; *Dobereiner's triad* and magnesium, zinc, cadmium, and mercury.

That which is most out of its place is beryllium, which has no especial resemblance to any other member of the entire group. As we have already seen, it was doubtful whether its atomic weight should be 9.1, or half as much again. Its chemical properties alone were not decided enough to give any definite indication as to the true formula of its simplest oxide.

Calcium, strontium, and barium, again, form one extremely well-defined group, showing the variation in properties, such as the solubility of their sulphates *v. analysis of the group.* and of their hydrates, which arranges them in order as well as contrasts them with the other half of the series. Magnesium, zinc, and cadmium also form

a well-marked group, in spite of the different groups into which they fall in ordinary qualitative analysis. Their soluble sulphates and insoluble oxides mark them off rather sharply from the calcium group. The elements themselves strongly resemble one another in general physical properties, as in volatility. Mercury is in many respects more like the members of some of the other groups, and from a general knowledge of its salts and other compounds, one would undoubtedly have placed it along with copper and silver. The reasons (apart from atomic weight) for placing copper in the first series hold with equal force for mercury.

In the third series we have very few elements whose properties have been sufficiently studied, as several are of great rarity. The first and second members point to a tendency to act into two groups, as in the groups we have already considered. They, however, differ more than the previous groups, which were entirely made up of well-defined metals, but boron has in no way any metallic properties, and the only apparent justification of their being placed together is that their oxides are of the form M_2O_3 . It is very doubtful whether aluminium is a real triad, probably only a pseudo-triad, that is, two atoms take six of chlorine, but they must be united to one another, hence are really treated as $Al - Al$, Al_2Cl_6 corresponding to C_2Cl_6 much more strictly than Al_2O_3 to B_2O_3 . Boron unites with hydrogen to form a hydride, BH_3 , and resembles carbon and silicon in the variations of its specific heat as well as in its allotropic modifications.

Aluminium, on the contrary, is a very well defined metal, dissolving readily in dilute hydrochloric acid

with evolution of hydrogen. Its oxide undoubtedly acts as an acid oxide to strong bases, such as the oxides of sodium and potassium, forming soluble salts, from which it may be expelled by carbonic acid.

The fourth series are well-marked tetrads, of which the stable oxides usually have the formula MO_2 , and chlorides MCl_4 . They are likewise more or less divisible into two groups, which we might characterise as metallic and non-metallic, germanium, tin, and lead being undoubtedly metallic. Silicon, which ought to be one of this group, possesses far more of the tendencies of the remaining members. Carbon is remarkable for its great power of combining with itself to form, as it were, the very complicated skeletons of innumerable organic substances. The silicates, from their complicated constitution, indicate a similar tendency to form apparently large molecules.

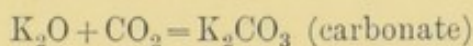
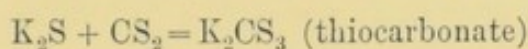
Tin and lead each form two well-defined oxides, corresponding in formula to CO and CO_2 . In the case of lead, however, we can hardly call the dioxide a basic oxide. It rather behaves as an acid forming oxide, and combines with basic oxides to form salts. The monoxide indicates likewise the same tendency. Both oxides of tin act as anhydrides, forming stannites and stannates, besides acting as bases and giving rise to stannous and stannic salts. Titanium dioxide, as rutile, is isomorphous with tin dioxide as cassiterite. The fluotitanates very much resemble the fluosilicates.

In the fifth series we have perhaps got the best natural group in the whole table, although separable, as in the other series, into two groups consisting respectively of the alternate members ; yet, as a whole, their

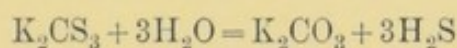
points of similarity are so strongly marked as to have indicated their belonging to the same group without the periodic law. This is especially seen in the formulæ of the oxides M_2O_3 and M_2O_5 , and their compounds with bases. The isomorphism of the vanadates with the phosphates and arsenates was one of the reasons for selecting 51 as the atomic weight of vanadium although the vapour densities of the oxychloride and the tetrachloride point conclusively to the same number. The existence of a tetrachloride, and especially one stable in the gaseous condition, is exceptional in this group, which are well-marked triads or pentads. The hydrides of the form MH_3 tend to combine with acids to form salts by direct addition. This is rendered more apparent in the compound phosphines, arsines, &c., as $P(CH_3)_3$, $As(C_2H_5)_3$, &c., than in the ordinary hydrides, although phosphonium iodide, PH_4I , is readily prepared, as may be also PH_4Cl under considerable pressure and at a low temperature. The pentachlorides, as phosphorus pentachloride and, what is of the same type, ammonium chloride, when volatilised tend to break up into molecules of the type $MH_3 + H_2$, as $NH_4Cl = NH_3 + HCl$, and $PCl_5 = PCl_3 + Cl_2$.

Series VI. is, again, formed of two more or less well-defined groups, in which we have the well-known group of the three similar elements with progressive properties—sulphur, selenium, and tellurium. For some time the atomic weight assigned to tellurium kept it out of its place, as it was taken as 129 until Brauner redetermined it, and pointing out the errors in previous determinations showed it to be about 125. Oxygen, and sulphur with its congeners form definite compounds of

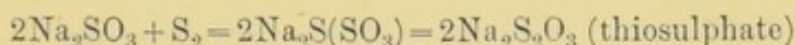
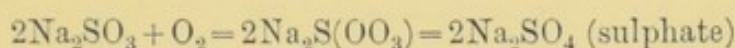
the type MH_2 , the other series forming chlorides of the type MCl_2 , MCl_3 , or M_2Cl_6 , and even MCl_6 ; but their strongest resemblance is in the tendency of all to form salts of the form K_2MO_4 , where M may be a member of either series, the sulphates and the chromates being, as already pointed out, strictly isomorphous, and thus linking the two series together. Sulphur and oxygen resemble one another very strongly in their compounds as



and by boiling a solution of the thiocarbonate



and



The oxychlorides of the series indicate more clearly than the simple chlorides the analogy between the metallic and the non-metallic groups.

The last regular series is far from complete as regards what we might say the classification requires, for we have only the well-defined family of the halogens and the alternate member manganese, which at first sight seems to be quite out of place; and it cannot be said, upon investigation, to show any strong resemblance, except that the perchlorates and permanganates of many metals are isomorphous, as $KMnO_4$ and $KClO_4$, or, more probably, $K_2Mn_2O_8$ and $K_2Cl_2O_8$. But we are unacquainted with any salts of the halogens of a similar constitution to the manganates, in fact, they correspond to the sulphates, the formula of potassium manganate being K_2MnO_4 , corresponding to K_2SO_4 . It has been

stated that almost colourless crystals of $\text{Na}_2\text{MnO}_4, 10\text{H}_2\text{O}$, isomorphous with $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, have been obtained; the existence of this salt is, however, disputed. As the ferrates resemble in every way the manganates, probably manganese should rather be grouped with iron and classed with those elements which are somewhat thorns in the side of the periodic arrangement of the elements. The great similarity of the halogens is very strongly marked in their hydrides and in their oxygen salts. Iodine tends to act also as a triad, as in ICl_3 .

From what has been said above, it is quite apparent that there is a distinct relation between the atomic weight and the physical and chemical properties of the elements, but it is equally plain that we must not carry our deductions from the atomic weight to too great a length. From the number of elements which are at present linked with those most certainly unlike them, we can hardly suppose we have yet got the best possible classification. In the above remarks very little notice has been taken of the rarer elements, many of the properties of which have not been investigated sufficiently. The classification of Mendelejeff has undoubtedly been very much strengthened by the discovery of three new elements since he enunciated his periodic law, and by his foretelling the discovery of three elements to fill gaps in the series, and of which he predicted the atomic weight, the density, and general physical and chemical properties of each. These three elements are scandium, gallium, and germanium, which he termed respectively, *eka-boron*, *eka-aluminium*, and *eka-silicon*. It is noteworthy that the discoverer of gallium, Lecoq

de Boisbaudran, at first attributed to it the density of 4·7, whilst Mendelejeff predicted 5·9 for his eka-aluminium; but when purer specimens were obtained 5·96 was found to be its true density. Nilson assigned to scandium the atomic weight, 170, from a determination with impure material, and Cleve showed it must be about 45. On further investigation Nilson proved it to have the atomic weight of 44.

A further support, as above mentioned, was derived from the revision of the atomic weight of tellurium by Brauner, the number formerly taken as its atomic weight, 129, placing it on the wrong side of iodine.

CHAPTER V.

CLASSIFICATION OF COMPOUNDS—ACIDS, BASES, SALTS.

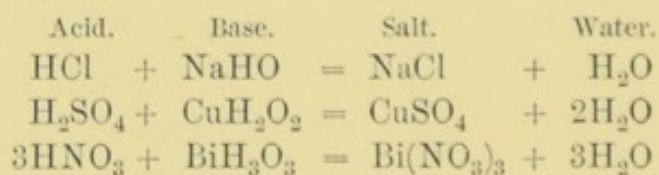
AMONG the commoner compounds which occur in everyday life, three classes stand out prominently—in fact, the majority of inorganic compounds may be regarded as belonging to one of these three. The three classes are respectively acids, bases, and salts.

Compounds of all the elements with oxygen are known with one exception—viz., fluorine. Most of these again combine with water to form hydrates. Some of these hydrates are termed acids, some bases.

Those elements which yield basic hydrates are termed *metals*. Those which yield none but acids are called *non-metals*.

An *acid* may be defined as a compound of hydrogen with an electro-negative element, or group of elements, the hydrogen being replaceable either entirely or in part by a metal when presented to it in the form of a *hydrated oxide or base*, a *salt* and *water* being produced.

Examples :—



The properties of an acid are, as a rule, sufficiently marked. It possesses a sour taste, turns vegetable blues

(such as litmus) to red, corrodes metals such as iron and zinc, generally with evolution of a gas. A base, on the other hand, if soluble in water, has a bitter taste, restores again the blue colour to the vegetable colour reddened by acids.

Amongst the earliest quantitative experiments on acids and bases are those of Homberg already referred to, who endeavoured to determine the equivalents of the acids by taking a certain weight of potassium carbonate, and neutralising it with various acids, and weighing the dry salt resulting from the action. About eighty years after, one of the last of the alchemists, Wenzel, was the first to give an explanation of the constitution of salts, and to enforce it by accurately performed experiments, and conclusions justly drawn from them. To Wenzel is due the idea of equivalency in chemical reactions, and the fundamental experiment from which his researches and deductions sprung was one well known before his time. If solutions of calcium nitrate and potassium sulphate are mixed, we have a double decomposition taking place resulting in the formation of calcium sulphate (insoluble) and potassium nitrate. The solution resulting from the reaction is neutral, like those before the reaction.

Two strong acids, sulphuric and nitric, were there, as well as the two powerful bases, potash and lime. Before the reaction the sulphuric acid was united to the potash, and the nitric acid to the lime. After the reaction the sulphuric acid found exactly enough lime to neutralise it, and the nitric acid likewise the correct amount of potash. Wenzel explained this fully by determining the composition of the four salts under con-

sideration, and the proportion in which they reacted on one another. He found that 123 parts of lime, (CaO) , yielded 363 parts of calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, and therefore united with 240 parts of nitric acid, (N_2O_5) ; and he found also that 240 parts of sulphuric acid, (SO_3) , were neutralised by 162.5 parts of lime, whence he calculated that 123 parts of lime ought to require 181.5 parts of sulphuric acid. But he had also determined that 240 parts of sulphuric acid required 290.4 of potash, (K_2O) , therefore he said 181.5 should require 220 parts of the potash and form 401.5 parts of potassium sulphate; and to completely precipitate the lime from 363 parts of calcium nitrate it ought to require the 401 parts of potassium sulphate. Now, on the precipitation of the 304.5 parts of calcium sulphate, he concluded that the 240 parts of nitric acid thus set free must unite exactly with the 220 parts of potash simultaneously liberated, and proved by an analysis that this was so, for he found that 240 parts of nitric acid united with and neutralised $222\frac{2}{3}$ parts of potash. All things considered, the experiments and analyses of Wenzel were wonderfully accurate. His researches were published when the chemists of the day were laying the foundations of modern chemistry on the ruins of the phlogistic theory. As his experiments seemed to have little to do with the battle then raging, they were speedily forgotten, and not until fifteen years afterwards another German chemist, Richter, returned to and extended the observations of Wenzel, although his experiments were not nearly so accurate.

He for the first time published a table of equivalents of bases and acids, which were of two kinds, the

quantity of various bases required to unite respectively with, for example, 1000 parts of sulphuric acid, and a corresponding one for the various acids with respect to bases, as 1000 parts of potash. He constructed a series of tables of this kind, overlooking the fact that one table could have given all the numbers just as well for all practical purposes by taking one as a standard, say 1000 parts of sulphuric acid, and referring all to that.

Further, however, he observed that when a metal put into a neutral solution of a salt precipitated another metal, the solution remained neutral, and practically from this, concluded that the weights of the oxides required to neutralise a given quantity of acid, contained the same amount of oxygen.

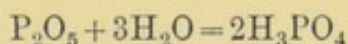
For a long time salts were regarded as consisting of an acid oxide (the oxide of a non-metal) united to a basic oxide (the oxide of a metal), and this even in spite of the fact that the typical salt, common salt or sodium chloride, contained no oxygen at all. When chlorine was proved to be an element and to contain no oxygen, and when its relation to hydrochloric acid was clearly understood, this view could no longer be held, although for many salts and in studying many reactions this mode of regarding salts was long adhered to, and even now is the simplest way of looking at many changes. Acids were similarly regarded as compounds of water and an acid oxide.

When a current of electricity is passed through a solution of a metallic salt, the metal appears at one electrode and the salt radical at the other, and this is so whether the salt contains oxygen or not. Electrolysing copper chloride we get copper and chlorine, and copper

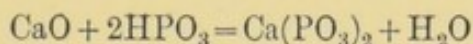
sulphate we get copper and the group (SO_4), which at once breaks up into oxygen and sulphur trioxide, which dissolving in the water forms sulphuric acid. An acid treated in the same way gives hydrogen where the salt would give a metal. An acid is, in fact, nothing but a salt of hydrogen, and if we change the definition of an acid above given so as to make it do for a salt we get—a salt is a compound of a metal and an electro-negative element or group of elements, oxygen alone being excepted.

Why is oxygen excepted? Obviously, from our definition, because it produces a base when it unites with a metal, hence a base may be defined as a salt whose electro-negative radical is oxygen; and we have seen that an acid is a salt whose electro-positive element is hydrogen, and further that when an acid and a base act on one another, a salt is produced, and at the same time, *water*. We may learn much from considering the question—Is water an acid, a base, or a salt? We shall best understand its position by considering some common reactions. Just as by placing certain metals in solutions of certain salts we may produce new salts, and the precipitation of the metals originally in solution, so by adding a base to a solution of a salt we may have the base in combination expelled and a new salt formed. Potassium hydrate added to calcium chloride gives calcium hydrate and potassium chloride, and calcium hydrate added to ferric chloride will give ferric hydrate and calcium chloride. We call potassium hydrate a stronger base than calcium hydrate, and it again is said to be stronger than ferric hydrate. When a stronger base is added to a salt of a weaker one, the weaker base is expelled. In the same way with acids, if acetic acid be

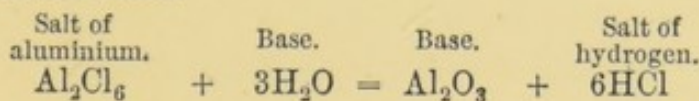
added to potassium sulphate and the mixture distilled, we do not get sulphuric acid and potassium acetate ; but if we begin with these and distil we get acetic acid and potassium sulphate. Sulphuric acid is said to be a stronger acid than acetic, and by pouring acetic acid on sodium carbonate, we get sodium acetate and carbonic acid, showing that acetic is stronger than carbonic acid. When a stronger acid is added to a salt of a weaker one, the weaker acid is expelled. How does this help us with regard to water ? Acids are salts of hydrogen, and therefore water is the base, as it is the oxide of hydrogen. If we burn a non-metal, phosphorus, in air or oxygen, we get a white powder—phosphorus pentoxide, P_2O_5 . It is an acid oxide. It combines with water with evolution of much heat to form phosphoric acid, H_3PO_4 .



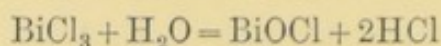
Now, if we try to separate again the water from the phosphoric acid by the aid of heat, we find it impossible. We can get some of it away and leave a new acid, analogous to nitric acid, metaphosphoric acid, HPO_3 , which may be regarded as formed from $P_2O_5 + H_2O = 2HPO_3$, but this last hydrogen remains. If we add, however, a base to it we expel the weaker *base*, water.



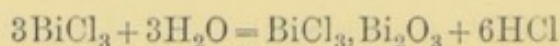
Water, then, may be regarded as a base. It ought, however, to be able to remove an acid from a salt and expel its base. If we add water to aluminium chloride, and evaporate to dryness, we get aluminium oxide and hydrochloric acid.



We have many cases in which it acts partially, as when water is added to bismuth trichloride we get bismuth oxychloride and hydrochloric acid.

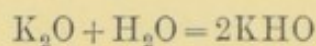


which may be written

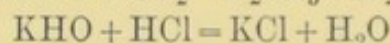
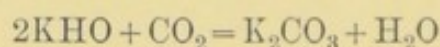


Does water ever act as an acid?

If we take a basic oxide such as potassium oxide, K_2O , and add water, just as in the case of phosphorus pentoxide we have chemical combination with evolution of much heat and a new body, potassium hydrate, KHO , produced, from which we cannot separate the water by heat alone.



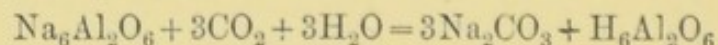
To do so, we must use an acid or an acid oxide.



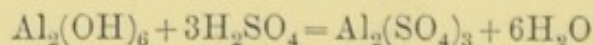
The *acid*, water, is expelled by the stronger acids according to our rule. Water is by no means the only oxide which behaves both as an acid and a basic oxide. Aluminium oxide is a very good example of another. In purifying bauxite, which is impure alumina, it is fused with sodium carbonate, and we have carbon dioxide expelled and sodium aluminate formed.



This is reversed in solution, for when carbon dioxide is passed into the solution, we have pure aluminium hydrate precipitated.



If we dissolve this precipitate in sulphuric acid we get aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$.



On adding to this, carefully, a solution of a powerful base, such as sodium hydrate, we get exactly the same precipitate that we obtained formerly with carbon dioxide, but now produced by a basic instead of an acid oxide; and if we continue to add sodium hydrate, the white precipitate will redissolve and form again sodium aluminate from which carbon dioxide will reprecipitate aluminium hydrate. Hence we see that no sharp line can be drawn between acids, bases, and salts, and that the conditions under which the reactions take place really determine whether a body shall function as one or other of these.

Acids are classified according to the number of hydrogen atoms in a molecule which can be replaced by metals. Those with one atom replaceable are termed monobasic, and of such acids we may instance hydrochloric, HCl ; nitric, HNO_3 ; acetic, $\text{HC}_2\text{H}_3\text{O}_2$; hypophosphorous, HPH_2O_2 .

Of dibasic, we have hydrosulphuric, H_2S ; sulphuric, H_2SO_4 ; tartaric, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$; and phosphorous, H_2PHO_3 .

Of tribasic, phosphoric, H_3PO_4 , and citric, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$.

To determine the class to which an acid belongs, we may find out by experiment how many salts it can form with a metal such as potassium. It is quite evident that we can have only one with a monobasic acid, HCl giving KCl , HNO_3 giving KNO_3 , $\text{HC}_2\text{H}_3\text{O}_2$ giving $\text{KC}_2\text{H}_3\text{O}_2$; but in a dibasic acid we have two atoms of hydrogen which may be replaced one by one, H_2S giving KHS and K_2S , H_2SO_4 giving KHSO_4 and K_2SO_4 , $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ giving $\text{KHC}_4\text{H}_4\text{O}_6$ and $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$. In tribasic acids we have a possibility of three salts, and so with phos-

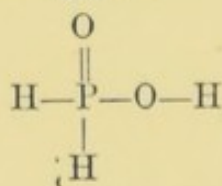
phoric acid, H_3PO_4 , we have KH_2PO_4 , K_2HPO_4 , and K_3PO_4 , and similarly for citric acid.

The formulæ of the three acids, hypophosphorous, phosphorous, and phosphoric, are respectively H_3PO_2 , H_3PO_3 , H_3PO_4 ; but as we can only get one hypophosphite of potassium, and it has the formula KPH_2O_2 , hypophosphorous acid is said to be monobasic although it has three atoms of hydrogen, only one of these being replaceable. Phosphorous acid similarly is dibasic, for we can obtain the salts KH_2PO_3 and K_2HPO_3 , but K_3PO_3 has not been obtained. Phosphoric acid, as above mentioned, gives all three salts.

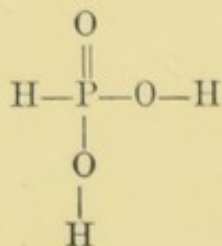
Another mode of determining the basicity of an acid is to determine the composition of the silver salt. Silver almost invariably turns out the whole of the replaceable hydrogen, and gives us a "normal salt." So that when we find the formula of silver hypophosphite is AgH_2PO_2 , we conclude that $(\text{H}_2\text{PO}_2)'$ is the salt radical of the hypophosphites; as silver phosphite is Ag_2HPO_3 , $(\text{HPO}_3)''$ is that of the phosphites; and as silver ortho-phosphate is Ag_3PO_4 , $(\text{PO}_4)'''$ is the salt radical of the ortho-phosphates.

It is quite evident, then, that in a molecule of the first two acids the hydrogen atoms are not all alike in function, and as phosphorus may be represented as a pentad, we may formulate the acids thus:—

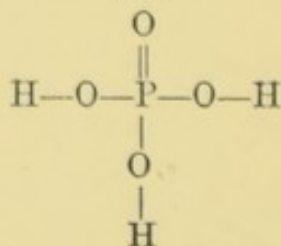
Hypophosphorous
acid.



Phosphorous
acid.



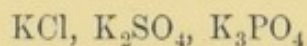
Phosphoric
acid.



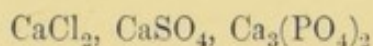
only those hydrogen atoms which are united to the phosphorus by means of oxygen, being replaceable by metals.

Salts are classified as normal salts, acid salts, and basic salts. Some salts are termed neutral, but these must not be confounded with normal salts, as is too often done.

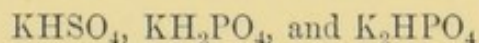
When we have all the replaceable hydrogen of an acid exchanged for a metal, we get a normal salt, as



or

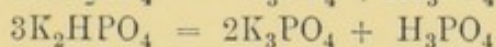
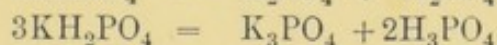
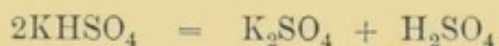


but when we have only part of that hydrogen replaced by a metal, an acid salt results, as

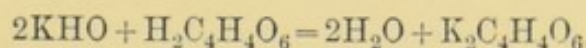


This quite irrespective of its action on litmus, for as long as replaceable hydrogen remains, it is still a salt of hydrogen, and a salt of hydrogen is an acid.

Acid salts may be regarded as composed of free acid and normal salt.

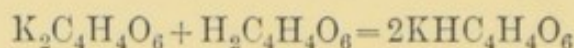


This is very readily seen by taking a solution of tartaric acid, dividing it into two equal parts, neutralising one carefully with potassium hydrate, when we get normal *and* neutral potassium tartrate.

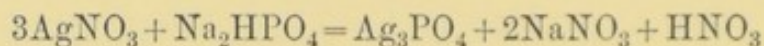


Add now the other part of the tartaric acid solution, which contains exactly the same amount of tartaric acid

as was neutralised, when we get a white precipitate of potassium acid tartrate, or bitartrate, as it is often termed.



Common sodium phosphate, Na_2HPO_4 , is an acid salt by constitution, although slightly alkaline in its reaction towards litmus. Its acid constitution is readily demonstrated by adding to its solution one of silver nitrate, which is also quite neutral, when a yellow precipitate of silver phosphate (normal) is produced along with the nitrates of sodium and hydrogen.



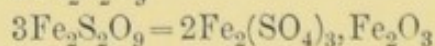
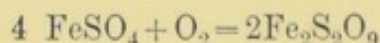
Basic salts in like manner may be regarded as compounds of the normal salt with some of the base; or we may define them as a base whose oxygen is only in part replaced by the salt radical of the acid.

Bismuth oxide is Bi_2O_3

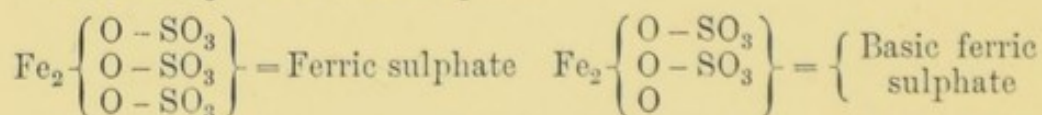
Bismuth nitrate is $\text{Bi}(\text{NO}_3)_3$

Bismuth basic nitrate is BiONO_3 or $(\text{Bi}(\text{NO}_3)_3, \text{Bi}_2\text{O}_3)$

When green ferrous sulphate absorbs oxygen (as it does while being dried before distillation in the manufacture of Nordhausen sulphuric acid), it becomes a basic ferric sulphate having the formula $\text{Fe}_2\text{S}_2\text{O}_9$.



$\text{FeO} - \text{SO}_3$ = Ferrous sulphate



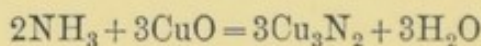
Neutral salts are those which are neutral to test-papers, such as litmus, and are those formed by the union of a strong acid with a strong base, or of a weak acid and a weak base, but with a strong acid and a weak base the

normal salts have always an acid reaction to litmus, whilst normal salts formed from a weak acid and a strong base have an alkaline reaction.

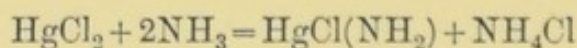
The salts of potassium, sodium, (ammonium), barium, strontium, calcium, magnesium, manganese, and silver with strong acids have a neutral reaction, all other ordinary metals giving salts with an acid reaction. If we take ferric chloride and try to neutralise it with potassium hydrate, we do not get it neutral till we have removed all the iron from the solution. We can prepare ferric chloride from pure iron and pure chlorine, and obtain the solid free from every trace of acid; yet, when dissolved in pure water, the solution very rapidly turns turbid and precipitates ferric hydrate, and a corresponding amount of hydrochloric acid remains free in solution, and every time we neutralise this hydrochloric acid a fresh quantity of ferric hydrate and hydrochloric acid are reproduced as long as any ferric chloride remains in solution.

Inorganic compounds of other classes exist which also may be looked upon as salts. When considering isomorphism the group of spinelles was taken as an example; they were shown to be compounds of two oxides, the one which contained relatively the smaller proportion of oxygen acting as the base, as in spinelle, $\text{MgO}, \text{Al}_2\text{O}_3$, which might be called a magnesium aluminate, the magnesia being the basic oxide. It is not the true aluminate, however, which would be $3\text{MgO}, \text{Al}_2\text{O}_3$. Many oxides which have no corresponding series of salts are constituted in a like manner. Peroxides, like manganese dioxide, MnO_2 , are termed indifferent oxides, but generally, however, they indicate a tendency to act as feeble acid oxides.

Many compounds, such as nitrides, sulphides, phosphides, and other binary compounds, which, though logically, and according to our definition, are salts, are yet classed separately. If we look at the nitrides we may see, perhaps, why this is so. We give the name hydrosulphuric acid to the common compound of sulphur with hydrogen, and usually regard the corresponding compounds—the sulphides—which we obtain by double decomposition or otherwise, as salts, although the solution of hydrosulphuric acid possesses a very feeble acid reaction. In the case of ammonia, however, which is the corresponding nitrogen derivative, we have a powerfully basic body, which is capable of neutralising the strongest acids, but by its reactions with the oxides of metals we may obtain many of the nitrides. By passing at a carefully regulated temperature ammonia gas over copper oxide we get a salt and water formed.



Copper nitride, Cu_3N_2 , is a powder of an olive-green colour, and may be used as a source of pure nitrogen as it readily decomposes into its elements at a higher temperature. By adding ammonia to a solution of mercuric chloride we get $(\text{NH}_2)'$ taking the place of $(\text{Cl})'$.



This may be regarded as an evidence of its acting as a tribasic acid, but of this better examples are the three compounds of the alkali metals formed by passing dry ammonia gas over the metal at a high temperature when we obtain with sodium NH_2Na , NHNa_2 , and NNa_3 .

Phosphine, PH_3 , which is quite analogous to ammonia, precipitates copper phosphide, Cu_3P_2 , from a solution of

copper sulphate; and stibine, SbH_3 , precipitates silver antimonide, SbAg_3 , when passed through a solution of silver nitrate, a reaction used in the separation of antimony and arsenic in qualitative analysis.

As we have seen with the classification of the elements, we can hardly in any case draw hard and fast lines of separation between groups, and that the two classes of substances, acids and bases, which are usually regarded as of the most opposite nature, gradually merge into one another, and that many substances may act as either, according to the circumstances. We also saw that in the placing of the elements in electrochemical order we might have one element either positive or negative to another, according to circumstances. As a general rule, however, our definitions, as above given, hold, viz., that the oxides of the metals act as bases, and that the lower the proportion of oxygen the stronger the base, that the compounds of hydrogen with the non-metals, and with electro-negative radicals, which consist usually of one of the non-metals along with more or less oxygen, act as acids.

Lavoisier gave to the gas previously known by the names of "vital air" and "dephlogisticated air," that of oxygen, as he supposed it to be not only a necessary constituent of every acid, but in fact, what its name indicates, *the* acid producer. Although many well-known acids are quite free from oxygen, and do not even require the presence of water, yet, as we shall see, especially when we consider the compounds of carbon, that the name is by no means inappropriate. If we look at the oxides of many of the elements, we see this very plainly: take as an example the oxides of manganese—

Manganous oxide, MnO , is a powerful base, neutralising the strongest acids.

Trimanganic tetroxide, $\text{Mn}_3\text{O}_4 = \text{MnO}, \text{Mn}_2\text{O}_3$.

Manganic oxide, Mn_2O_3 , a very weak base.

Manganese dioxide, MnO_2 , an indifferent oxide, tending to combine with bases, as in Weldon mud, which may be regarded as $\text{CaMnO}_3 = \text{CaO}, \text{MnO}_2$.

Manganic anhydride, (MnO_3) , forms a feeble acid, unknown in the free state.

Permanganic anhydride, (Mn_2O_7) , forms a strong acid and well-defined salts.

Or those of nitrogen—

Nitrous oxide, or hyponitrous anhydride, N_2O , gives salts as AgNO , very unstable.

Nitrous anhydride, N_2O_3 , gives salts as AgNO_2 , stable.

Nitric anhydride, N_2O_5 , gives salts as AgNO_3 , very stable.

With chlorine we have—

Hydrochloric acid, HCl , a strong acid.

Hypochlorous acid, HClO , a very weak acid.

Chlorous acid, HClO_2 , a weak acid.

Chloric acid, HClO_3 , a fairly strong acid.

Perchloric acid, HClO_4 , a very strong acid.

CHAPTER VI.

CLASSIFICATION OF COMPOUNDS—CARBON COMPOUNDS.

THE compounds of carbon are usually treated as if more or less separated from the compounds of all other elements. This is due, as previously pointed out, to the remarkable way in which carbon unites with itself to form the framework of compounds of very complex nature, and as many of these bodies were first obtained from plants and animals or their remains, the term organic chemistry came to be applied to the chemistry of the carbon compounds. In all of these, with one solitary well-defined exception, carbon may be regarded as a tetrad; but in that one exception, carbon monoxide, carbon behaves as a dyad. This is readily seen by the tendency of carbon monoxide to take up an atom of oxygen or a molecule of chlorine, and the carbon then becomes a tetrad, the compounds having the formulæ CO_2 and COCl_2 . There is no doubt whatever regarding the formula of carbon monoxide, the ratio of its specific heats, and the great resistance it offers to liquefaction, as well as its low vapour density, clearly point to CO as its formula. In all other cases, as we have above stated, carbon may be regarded as a tetrad, but not necessarily, however, existing in combination with other elements so as to satisfy this valency, for its atoms have the power of combining with one another singly, doubly, and trebly,

as it were, even when we have only two atoms of carbon along with hydrogen, as we see in the following compounds :—

Marsh Gas.	Ethane.	Ethylene.	Acetylene.
CH_4	C_2H_6	C_2H_4	C_2H_2

The following classes comprise most of the important compounds of carbon :—

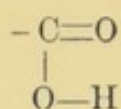
1. Hydrocarbons.
2. Alcohols.
3. Aldehydes.
4. Acids.
5. Ethers.
6. Amines.
7. Nitro-compounds.
8. Cyanogen compounds.
9. Organo-metallic bodies.

The Hydrocarbons contain no elements but carbon and hydrogen, and all other organic substances may be regarded as derived from them. The hydrocarbon radicals or residues formed by removing 1, 2, or 3, &c., atoms of hydrogen correspond respectively to the metals uniting with 1, 2, or 3, &c., atoms of chlorine or monad groups, such as (NO_3).

The Alcohols contain the three elements, carbon, hydrogen, and oxygen, and are analogous to the metallic hydrates. They are formed by the union of the monad radical (or water residue) hydroxyl, (OH), with the hydrocarbon radicals.

The Aldehydes contain the same elements as the alcohols, from which they differ in having one or more pairs of atoms of hydrogen less. They are powerful reducing agents, and pass by oxidation into

The Acids, which contain an oxygen atom more than the aldehydes for every two hydrogen atoms which the alcohol lost in becoming an aldehyde. They may be regarded therefore as alcohols which have one oxygen atom for two atoms of hydrogen. This oxygen atom is always united to the same carbon atom as that to which the hydroxyl group is attached. Hence we must have the monad group

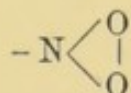


known as *carboxyl*, in all true organic acids.

The Ethers are the salts of organic chemistry, and may be regarded as formed by the union of a hydrocarbon radical with the salt radical of an acid, or as produced by the interaction of an alcohol (base) with an acid, an ether (salt) and water being produced. They are termed simple or compound, according as the salt radical is an element or a group of elements.

The Amines, as their name indicates, are bodies like ammonia, containing nitrogen as their nucleus, and which unite directly with acids to form salts like those of ammonium.

The Nitro-compounds are derived from hydrocarbons and contain one or more monad groups



in place of an equal number of hydrogen atoms. This group must not be confounded with the salt radical of the nitrites, which is ($-\text{O}-\text{N}=\text{O}$).

The Cyanogen Compounds contain the monad radical cyanogen alone, either as $(-\text{N}\equiv\text{C})'$ or $(-\text{C}\equiv\text{N})'$, or in a more complex form with the addition of oxygen, sulphur, &c.

The Organo-metallic Compounds may be regarded as ethers, in which we have a metal taking the place of the electro-negative group. They are of very great service in investigating the structure and in building up many organic bodies.

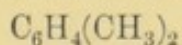
One of the first and most obvious consequences of the property which carbon has of uniting with itself and other elements is that we may have many substances with exactly the same empirical formula, but having very different chemical constitutions and properties. Many such bodies are known; but, in the first place, we will divide them into two groups—(1) those having the same molecular weight, as well as composition, which are termed Isomeric bodies; and (2) those having different molecular weights, but the same relative composition, which are termed Polymeric bodies.

We have very few examples of either class amongst inorganic compounds, but we may instance oxygen, O_2 , and ozone, O_3 , as a simple well-defined case, also NO_2 and N_2O_4 , the former a dark coloured gas, and the latter a colourless one, which change into one another according to the temperature. The anhydride of true hyposulphurous acid, H_2SO_2 , which is SO , that of thiosulphuric acid (wrongly called hyposulphurous), $\text{H}_2\text{S}_2\text{O}_3$, which is S_2O_2 , and that of pentathionic acid, $\text{H}_2\text{S}_5\text{O}_6$, which is S_5O_5 , afford us another example of polymerism. We have likewise the same occurring in the varieties of stannic and similar acids, stannic acid being H_2SnO_3 , and

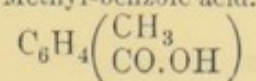
metastannic acid, $\text{H}_2\text{Sn}_5\text{O}_{11} + 4\text{H}_2\text{O}$, in which we have respectively SnO_2 and Sn_5O_{10} as the anhydrides, and the solids as H_2SnO_3 and $\text{H}_{10}\text{Sn}_5\text{O}_{15}$. Isomerism in the elements is termed allotropy, but we can seldom distinguish between that and polymerism as in the case of oxygen and ozone, phosphorus, red and yellow, carbon as diamond, graphite, and charcoal, in all of which we have different chemical and physical properties; we have undoubtedly in each case only the one substance, but the molecular weights of the various modifications, except in the case of oxygen and ozone, are unknown. It is most probable, in the case of the elements, that the difference in properties is due to a difference in the arrangement of the atoms into larger and smaller molecules.

Isomeric substances are usually divided into two groups—Isomeric bodies, strictly so called, and Metameric bodies. Isomeric bodies not only have the same molecular weight, but with similar reagents give rise to similar products, thus indicating great similarity of structure. Metameric bodies, however, when treated with similar reagents, give rise to entirely different products, and thus have entirely different structures, although having the same molecular weight. A very good example of isomerism is afforded by some of the hydrocarbons derived from benzene. We have three isomeric hydrocarbons, called dimethyl-benzene, having the empirical formula C_8H_{10} , which, when carefully oxidised, give rise to three monobasic acids, each a methyl-benzoic acid, and when further oxidised each gives a phthalic acid, which is dibasic.

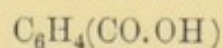
Dimethyl-benzene.



Methyl-benzoic acid.

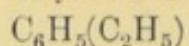


Phthalic acid.

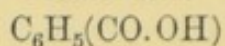


Another hydrocarbon, having the same composition and molecular formula, ethyl-benzene, when oxidised gives rise to a monobasic acid, benzoic acid, and we have only the one stage in the oxidation.

Ethyl-benzene.



Benzoic acid.



The three dimethyl-benzenes are then said to be truly isomeric, but the ethyl-benzene is only metameric with them.

Although it has been assumed that the student understands and is quite familiar with the use of ordinary molecular formulæ, it may be as well, while dealing with the subject, to point out their true use and meaning. In all *chemical* reactions it is only the individual molecules with which we have to deal. Each true formula represents a definite individual quantity of a substance which we term a molecule, which has perfectly well-defined properties, especially important being its mass and volume relations. The formula ought, therefore, never to be used to represent indefinite quantities of the substance; and the slovenly use of the *formula* for the *name* of the substance is particularly reprehensible in a science which has any pretensions to accuracy and to a scientific nomenclature. Three examples, taken at random from a recently-published book, will illustrate our meaning:—

(1) “Drop a small piece of K into a basin of H_2O The K must be very small, and the experiment should not be watched at too close a range. The H burns, united with O of the air. The purple colour is imparted by the burning, or oxidation of small particles of K.”

(2) “Put a Ag coin, such as a threepenny-bit, &c.”

(3) "Test it with burning S. NO is not a supporter of C and S combustion. Put a small bit of P in a deflagrating spoon, &c."

Besides such parodies of scientific language, however, other errors are to be guarded against. The equation $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$, representing the decomposition of potassium chlorate by heat, in which each term consists of a definite number of molecules, is often written $\text{KClO}_3 = \text{KCl} + \text{O}_3$ or $\text{KClO}_3 = \text{KCl} + 3\text{O}$, both of which are wrong, the first representing 122.5 grams of potassium chlorate as giving 22.4 litres of ozone, and the second (if it represents anything in the way of volume) as giving 67.2 litres of oxygen (?). Each term of an equation ought to refer to a definite number of *molecules*, not of atoms as such.

In inorganic chemistry we have but little necessity to introduce a more developed notation than that commonly in use. Each substance has its own formula, and but little doubt can arise as to what is meant. Our ordinary notation, it is true, gives but little information as to how the atoms are arranged in each individual molecule. From what has been said above, it is quite apparent that when we have four compounds having the formula C_8H_{10} , and no less than 799 of the formula $\text{C}_{13}\text{H}_{28}$, we require a notation representing in some concise way as many as possible of the differences existing amongst such compounds. We have seen already that Dalton used symbols for his atoms, and represented the molecules by arranging the atoms together in groups.

A system of the same nature, and based on the atomicity of the elements, is in almost universal use

amongst chemists at the present time, and although not in any way indicating the arrangement of the atoms in space, has proved of inestimable value in directing research towards the most probable methods of building up bodies from simple constituents. In this notation, which we shall use so much in the present chapter, each atom is represented as having as many lines drawn from it as it combines with atoms of hydrogen or other monad elements, so that we would represent

Hydrochloric acid, HCl , as . . . $\text{H}-\text{Cl}$

Water, H_2O , as . . . $\text{H}-\text{O}-\text{H}$ or $\text{O} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{H} \end{array}$

Ammonia, NH_3 , as . . . $\text{H}-\text{N}-\text{H}$ or $\text{N} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{H} \\ | \text{H} \end{array}$

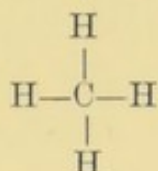
Marsh gas, CH_4 , as . . . $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$

Ammonium chloride, NH_4Cl , as . . . $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{H}-\text{N}-\text{H} \\ | \\ \text{Cl} \end{array}$

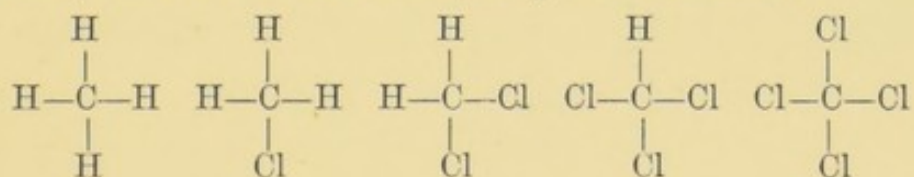
Phosphorus pentachloride, PCl_5 , as . . . $\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{Cl}-\text{P}-\text{Cl} \\ | \\ \text{Cl} \end{array}$

The graphic formula of a compound, as it is often termed, may be defined as "a summary of the reactions of the compound," and as such alone it ought to be used. An ingenious extension of the theory, so as to include not

only the reactions but to indicate in some degree the probable arrangement of the atoms in space, has been brought forward by Le Bel and van't Hoff. In the meantime we will content ourselves with the ordinary graphic formulæ. We write marsh gas or methane, CH_4 , thus

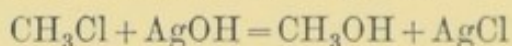


as all the reactions of marsh gas seem to indicate that the hydrogen atoms are of equal value and power, and that all are united directly to the carbon atom. When we act upon marsh gas with chlorine we have no addition compounds formed but only those of substitution—that is, the carbon does not at any time take more than four monad atoms; that if a chlorine atom becomes united to the carbon, it is at the expense of one of the hydrogen atoms, which must relinquish its hold on the carbon whatever the nature of its hold may be. We thus get a series of compounds— CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 , which, when more extended, may be written as

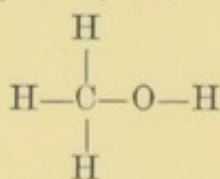


Now we only know one compound corresponding to each of these formulæ. Had we known four compounds having the formula CH_3Cl , we would have concluded that the chlorine and hydrogen atoms were differently united to the carbon in each case. As we only know one of each of these compounds, and not the slightest indication of even two varieties of any of them, we

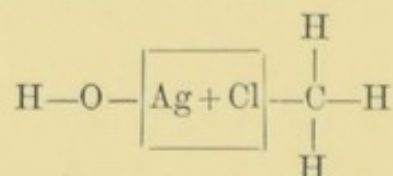
believe we are quite entitled to assume that there is no difference whatever in the mode in which the carbon is united to each of the hydrogen atoms. Carbon is then clearly a tetrad element, but it does not follow that a compound containing as its nucleus one carbon atom may not contain more than four other elements in its molecule, but that not more than four atoms of any kind can be united *directly* to any carbon atom. A very simple example of this is methyl alcohol, CH_3OH , which we can prepare from methane, CH_4 , by acting on it with chlorine so as to produce methyl chloride, CH_3Cl , and treat this so as to remove the chlorine (Cl) and replace it by hydroxyl (OH), as by means of moist silver oxide which behaves as AgOH .



Oxygen is a dyad, but (OH) is a monad radical, because it combines with one atom of hydrogen to form water; (OH) can replace or combine with one atom of hydrogen or chlorine, and in like manner (CH_3) is a monad radical, combining with one atom of hydrogen to form methane, and with one atom of chlorine to form methyl chloride. CH_3OH is, then, when written graphically,



being derived from the interaction of



The two monad residues which are left by the chlorine and the silver being exactly equivalent to one another

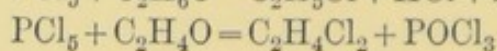
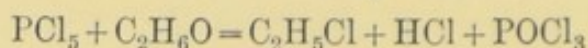
unite, so that although we could not make any direct addition to methane we may in this way increase the number of atoms which are *indirectly* attached to its carbon atom. We see, then, that the formulæ CH_4 and CH_4O are somewhat misleading, as the second naturally suggests an addition compound formed from the first, and that CH_4 , which we consider saturated, can have a dyad atom added to it. We may, without using graphic formulæ, convey to a certain extent at least an idea of the general structure of a compound.

All formulæ which exhibit more than the mere composition and molecular weight are termed *rational* or *constitutional* formulæ. Those which do no more than give the results of the simple analysis and the aggregates of the elements in a molecule of the compound are termed *empirical* formulæ.

To understand how we construct the rational from the empirical formula, which is all that we get from an ordinary analysis, we must say a few words on the action of reagents. The most important reagents in research of this kind are—phosphorus pentachloride, PCl_5 ; hydriodic acid, HI ; acetic anhydride $(\text{C}_2\text{H}_3\text{O})_2\text{O}$; oxygen usually applied in the form of a solution of chromic acid or potassium bichromate and sulphuric acid; nascent hydrogen from sodium amalgam; zinc methyl and ethyl; and dehydrating agents. To determine whether the oxygen in a compound is there as hydroxyl or not, phosphorus pentachloride is of very great use. If we treat, say, alcohol with it, we get from $\text{C}_2\text{H}_6\text{O}$, $\text{C}_2\text{H}_5\text{Cl}$; we see here that (Cl) has taken the place of (HO) in the alcohol, and that the residue of the alcohol is C_2H_5 , $\text{C}_2\text{H}_6\text{O}$ may be represented in all probability as $\text{C}_2\text{H}_5(\text{OH})$. If, how-

ever, we treat aldehyde, C_2H_4O , with the same reagent we get $C_2H_4Cl_2$, where we have the whole of the original carbon and hydrogen remaining, and one atom of oxygen replaced by two atoms of chlorine. From this we conclude that the oxygen is united directly to the carbon and to nothing else.

The two reactions are thus represented :—



Hydriodic acid in strong solution heated with many substances acts as a powerful reducing agent—that is, removing the negative elements because of the tendency for $2HI$ to break into $H_2 + I_2$; so that if we treat C_2H_6O with HI we first get C_2H_5I , then this reacting with HI gives $C_2H_6 + I_2$. We can thus in many cases get back to the hydrocarbon from which substances are derived. Oxidising agents enable us to convert many oxidisable bodies into oxidised products of simpler radicals as well as to add oxygen directly or to remove hydrogen. Hydrogen acts just in the opposite direction, removing oxygen and the halogens, and replacing them as a rule by equivalent proportions of hydrogen. The organo-metallic bodies, such as zinc methyl, are of great use in building up complex hydrocarbons, and of replacing the halogens by methyl and other radicals.

We referred in treating of the atomic weights of the elements to what we called the atomic volume, as well as to a connection between the molecular volume of substances of the same group. In both inorganic and organic chemistry this constant has proved of very great use in indicating the constitution, especially when the substance is examined in the liquid state. For the further con-

sideration of it, and of the action of organic bodies on light, see Chapter VIII.

In very much the same way as we have groups of elements which differ from one another either by a certain number, or a multiple of that number, which is very often 16, we have long series of very similar compounds which always, however, differ by 14, or multiples of it, no matter what class of compound it may be, and this 14 is made up of 1 atom of carbon = 12 and 2 atoms of hydrogen, forming the group (C H₂). From this similarity it has been thought not at all improbable that our elements will be broken up, and that the difference of 16 may either be due to an element or to a group of elements. We see this difference in

		Difference.
Lithium, Li	= 7	
		-16
Sodium, Na	= 23	
		-16
Potassium, K	= 39	
		-15·5 × 3
Rubidium, Rb	= 85·4	
		-15·9 × 3
Cæsium, Cs	= 133	
Magnesium, Mg	= 24·4	
		-15·6
Calcium, Ca	= 40	
		-15·8 × 3
Strontium, Sr	= 87·5	
		-16·5 × 3
Barium, Ba	= 137	

The hydrocarbons are arranged in series according to the proportion of hydrogen which they contain

relatively to the total amount possible. Those which contain the maximum amount are termed *paraffins* or saturated hydrocarbons, because of their inability to form any addition compounds with chlorine, &c. Only substitution compounds can be formed by them, an equivalent amount of hydrogen being removed for every equivalent quantity of either an element or group of elements introduced. It is to these saturated hydrocarbons that we in reality refer the great bulk of our other compounds, which may be considered as substitution compounds formed by removal of so many atoms of hydrogen from a member of the paraffin series, and their replacement by one or more simple or complex groups.

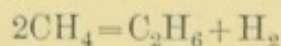
The hydrocarbons are classified as paraffins, olefines, and acetylenes, &c.

The paraffins have all the general formula C_nH_{2n+2}

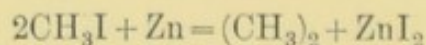
Methane, CH_4 ,	is the first,	n being	= 1
Ethane, C_2H_6 ,	„	second, n „	= 2
Propane, C_3H_8 ,	„	third, n „	= 3
Tetrane, C_4H_{10} ,	„	fourth, n „	= 4
Pentane, C_5H_{12} ,	„	fifth, n „	= 5
Hexane, C_6H_{14} ,	„	sixth, n „	= 6

and so on.

As already stated, we know only one methane having the formula CH_4 . Similarly, we know only one ethane, C_2H_6 , which may be formed from two molecules of methane by removing a molecule of hydrogen from them.

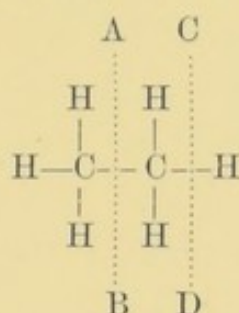


Also by removing the iodine from methyl iodide, CH_3I , by means of zinc, when the two methyl groups, (CH_3) , unite together and produce ethane or dimethyl.



It may be formed by adding water to zinc ethyl,

$\text{Zn}(\text{C}_2\text{H}_5)_2$, or replacing the chlorine in ethyl chloride $\text{C}_2\text{H}_5\text{Cl}$, by hydrogen, $\text{C}_2\text{H}_5\text{Cl} + \text{H}_2 = \text{C}_2\text{H}_5\text{H} + \text{HCl}$. $\text{C}_2\text{H}_5\text{H}$ is called ethyl hydride, and it is found to be identical in all its reactions with the gas from methyl iodide, so that at present we only know one ethane, whether we prepare it from methyl or from ethyl compounds. When we try to write its formula graphically, we find that we can only write it in one way, and that is



which equally well answers its description as dimethyl or ethyl hydride. We have only to imagine it composed of the two parts to the right and left of A B or C D respectively.

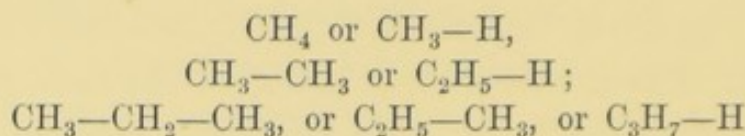
In the same way for propane, C_3H_8 , we write it



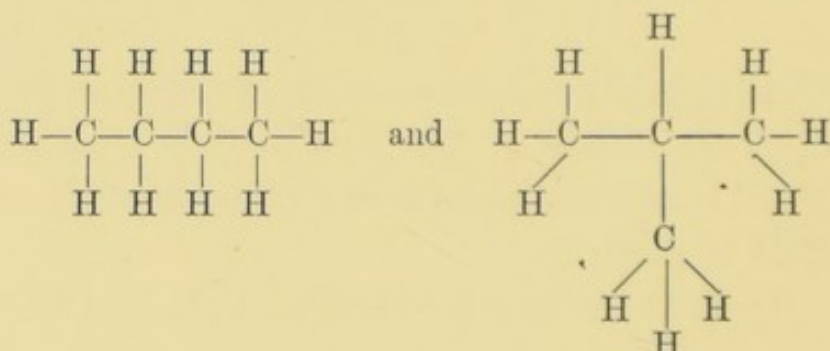
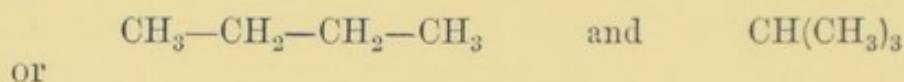
which we may call methyl ethyl, or propyl hydride, according as we think of it as divided by A B (and A' B') or C D (and C' D').

But as in the two previously considered, we can only arrange the hydrogen atoms and the carbon atoms in the

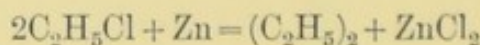
one way. The first three paraffins exist in only one form, which we may write briefly



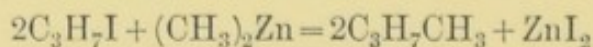
Every atom of carbon has got *at least* two hydrogen atoms united to it, but when we get to the fourth member of the series we can easily imagine more than one possible arrangement by which four carbon atoms may be completely saturated by ten hydrogen ones. Two are known, and only two are possible, according to our theory.



The first may be regarded as diethyl, and a hydrocarbon having the formula C_4H_{10} is got by removing the chlorine from ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$, by means of zinc.

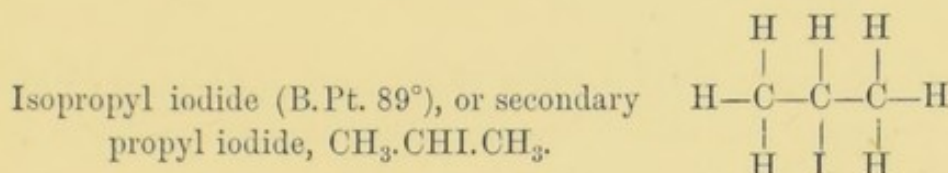
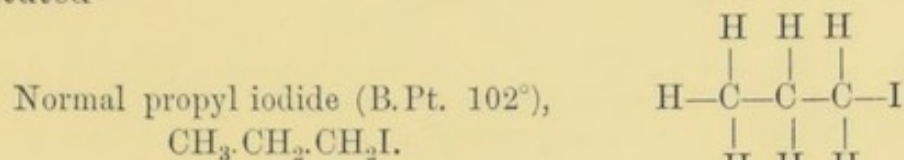


Although we have only one propane we have two propyl iodides, $\text{C}_3\text{H}_7\text{I}$, having different boiling points, &c., and if we treat them respectively with zinc methyl we get two corresponding tetranes (or butanes), C_4H_{10} .



One of the tetranes is identical with the diethyl as

above prepared. The two propyl iodides are thus constituted—

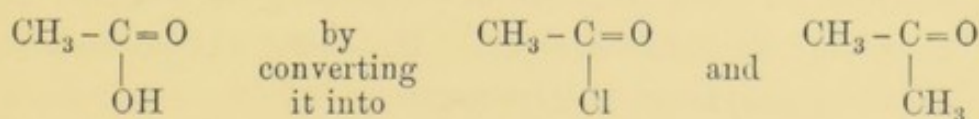


On replacing the iodine atom by the methyl group, (CH_3) , we obtain two tetranes corresponding to the two iodides. The tetranes boil respectively at $+1^{\circ} \text{C}.$ and $-17^{\circ} \text{C}.$

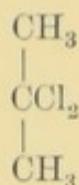
In the same way, from our theory, we would expect to have three pentanes. Investigation has shown that there are three pentanes at least, but more than three have not been produced. They are

- | | | | | |
|---|---|---|---|-----------------------|
| (1) $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ | . | . | . | B. Pt. 38° . |
| (2) $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$ | . | . | . | B. Pt. 30° . |
| (3) $\text{C}(\text{CH}_3)_4$ | . | . | . | B. Pt. 10° . |

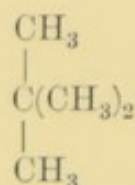
As in the other examples above given, we may prepare the first and second by combining the radical ethyl with the normal propyl and the isopropyl radicals respectively, by means of the above-mentioned iodides but using zinc ethyl instead of the methyl compound. They are evidently built on the same plan. The third form, however, is of a totally different type. It may be produced indirectly from acetic acid, which we shall afterwards see possesses the constitution



then exchange the oxygen atom for two chlorine atoms and we obtain



and for the chlorine get
two methyl groups
and we have



which is our third variety of pentane, boiling at 10°C .

Cayley calculated the numbers of hydrocarbons possible from one to thirteen carbon atoms, the carbons being fully saturated, and found :—

Number of Carbon Atoms.	Number of Paraffins.	Number of Carbon Atoms.	Number of Paraffins.
1	1	8	18
2	1	9	35
3	1	10	75
4	2	11	159
5	3	12	357
6	5	13	799
7	9

Have we any method of naming such compounds? is the next question. In the first place, we will consider how all hydrocarbons may be classified and designated, so as to give at least some idea of their constitution. No hydrocarbons are known in the free state which have an odd number of hydrogen atoms in their molecule. If we try to prepare C_2H_5 from $\text{C}_2\text{H}_5\text{Cl}$, its chloride, we get $\text{C}_4\text{H}_{10} = (\text{C}_2\text{H}_5)_2$, just as in trying to produce H from HCl we get invariably H_2 and not H; so we say the hydrocarbon, C_2H_5 , exists in combination, but is unknown in the free state.

PARAFFINS.		OLEFINES.		ACETYLENES.
C_nH_{2n+2}	I. (C_nH_{2n+1})	II. (C_nH_{2n})	III. C_nH_{2n-1}	IV. C_nH_{2n-2}
Methane. CH_4	<i>Methyl.</i> (CH_3)	Methene. (CH_2)	<i>Methenyl.</i> (CH)	...
Ethane. C_2H_6	<i>Ethyl.</i> (C_2H_5)	Ethene. C_2H_4	<i>Ethenyl.</i> (C_2H_3)	Ethine. C_2H_2
Propane. C_3H_8	<i>Propyl.</i> (C_3H_7)	Propene. C_3H_6	<i>Propenyl.</i> (C_3H_5)	Propine. C_3H_4
Tetrane. C_4H_{10}	<i>Tetryl.</i> (C_4H_9)	Tetrene. C_4H_8	<i>Tetrenyl.</i> (C_4H_7)	Tetrine. C_4H_6
Pentane. C_5H_{12}	<i>Pentyl.</i> (C_5H_{11})	Pentene. C_5H_{10}	<i>Pentenyl.</i> (C_5H_9)	Pentine. C_5H_8
Hexane. C_6H_{14}	<i>Hexyl.</i> (C_6H_{13})	Hexene. C_6H_{12}	<i>Hexenyl.</i> (C_6H_{11})	Hexine. C_6H_{10}
Heptane. C_7H_{16}	<i>Heptyl.</i> (C_7H_{15})	Heptene. C_7H_{14}	<i>Heptenyl.</i> (C_7H_{13})	Heptine. C_7H_{12}

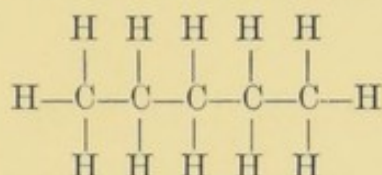
Odling has proposed the naming of the hydrocarbons somewhat as above, the hydrocarbons with even numbers of hydrogen atoms beginning with the paraffins having the characteristic letter (*a*), and for every loss of two hydrogen atoms taking the next vowel in its place. Taking the six carbon series as an example, we have hexane C_6H_{14} , hexene C_6H_{12} , hexine C_6H_{10} , hexone C_6H_8 , hexune C_6H_6 . For the unisolated hydrocarbons with an odd number of hydrogen atoms, the names end with the syllable -yl, so we would have hexyl, (C_6H_{13})', hexenyl, (C_6H_{11})'', &c. These, as a rule, are known as the alcohol or hydrocarbon radicals, and are the

most important radicals taken as a whole. They occur constantly in combination, although not known in the free state. Many of the hydrocarbons were known before this system of nomenclature was proposed, and retain their old names. Ethene, C_2H_4 , is heavy carburetted hydrogen, or olefiant gas, but more commonly known as ethylene, $(C_2H_3)'''$ is often known as vinyl, and C_2H_2 is generally known as acetylene. In every vertical series each member differs from that next to it by (CH_2) ; such series are termed *homologous*, but the members of each horizontal series have the same number of carbon atoms, and entirely different properties, and are termed *isologous*, whereas the members of a homologous series have very similar properties. Our table of hydrocarbons thus arranged corresponds in many ways with Mendelejeff's table of the elements. The paraffins are saturated, and only form compounds by substitution. The alcohol radicals, (C_nH_{2n+1}) , act as monads, as $(C_2H_5)Cl$, $(C_2H_5)_2O$. The olefines act as dyads, forming compounds as C_2H_4O , $C_2H_4Br_2$. The next series of radicals act as monads or triads, and give rise to compounds C_2H_3Br and $C_2H_3Br_3$, $C_3H_5(OH)$ and $C_3H_5(OH)_3$. The acetylene series act either as dyads or tetrads, $C_2H_2Cl_2$ and $C_2H_2Cl_4$ corresponding to $SnCl_2$ and $SnCl_4$, and so on.

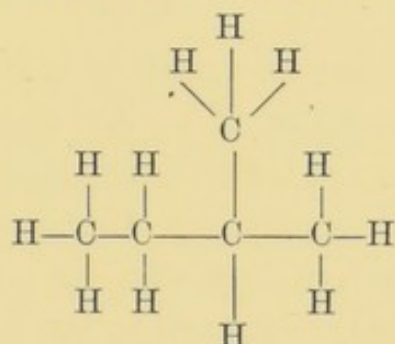
We have now seen how to group our hydrocarbons, and by testing with free bromine we are enabled to determine to which class they belong. With a paraffin there is no direct combination, and if we have any reaction, we get half of our bromine back in the form of hydrobromic acid; with an olefine, we get direct combination and have a dibromide formed but no hydrobromic acid, and with an acetylene we may

have a dibromide and a tetrabromide. But we have already seen that we may have many paraffins having the same molecular formula. These may be classified as:—

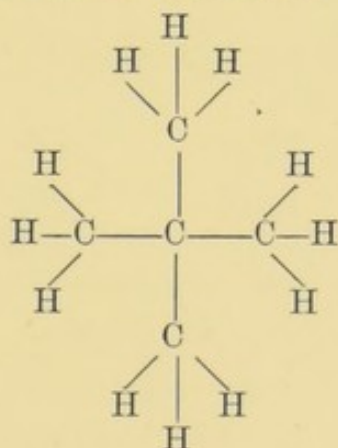
Normal Paraffins.—Those which have no carbon atom attached to more than two others, as



Isoparaffins.—Those which have one carbon atom united to three other carbon atoms, as

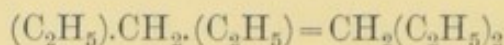


Neoparaffins.—Those which have one carbon atom united to four other carbon atoms, as

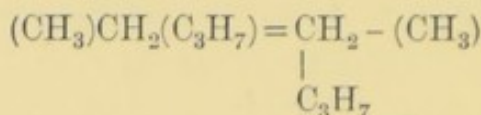


All may be regarded as derivatives of methane, and named accordingly, as in the above examples we may regard the normal pentane as $\text{CH}_3(\text{C}_4\text{H}_9)$, and call it

tetryl methane, having the radical tetryl introduced for one hydrogen, or



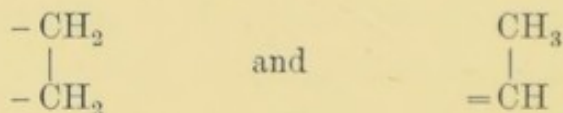
and call it diethyl methane, or



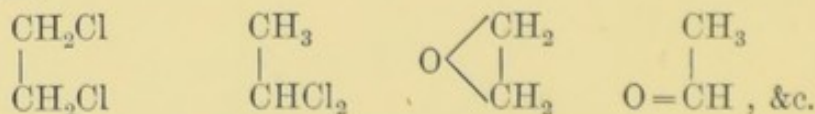
and call it methyl propyl methane. All the hydrocarbons made by combining these radicals so as to form these compounds are found to be but one and the same substance, and hence any of the above names is equally applicable to it.

The isopentane may be described as isobutyl methane, di-methyl ethyl methane, or methyl isopropyl methane, and the neopentane as tetra-methyl methane.

Although we have only one ethane we may have two ethenes, one called ethylene and the other ethylidene, but of these one only is known in the free state—



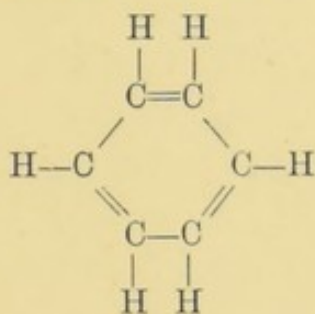
The chlorides, oxides, and other derivatives of each are known—



The problem of how to name these very numerous hydrocarbons without getting names too unwieldy is a difficult one, and in very many cases the simplest way seems to be to use the written graphic formulæ when precision is necessary.

All the hydrocarbons which we have considered have the carbon atoms in what may be considered a chain,

straight for the normal and *branched* for the other forms. In a very large number of hydrocarbons we have another form in which the carbon chain takes the form of a ring. Such hydrocarbons are termed *aromatic* in contradistinction to those we have already considered, which are termed *fatty*. The most important of the aromatic hydrocarbons, and the one which is the starting-point, just as methane is of the fatty series, is benzene, C_6H_6 , and its graphic formula is generally written in the form of a hexagon:—

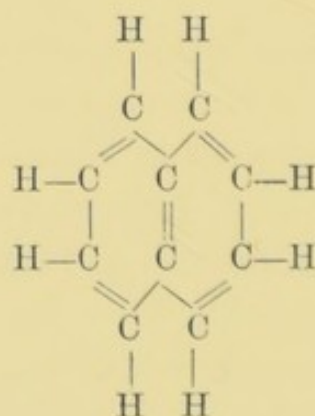


This is the famous formula proposed for benzene by Kekulé in 1865, the enunciation of which marks an epoch in the development of organic chemistry. The elegance and simplicity of the explanations furnished by it of the reactions of benzene and its derivatives give it such an advantage over other more recently proposed formulæ that we shall adopt it here.

When acetylene is heated it condenses to form a new substance, a liquid hydrocarbon, the vapour density of which is three times that of the original gas; hence its formula is C_6H_6 . This hydrocarbon will on no account, however, unite with more than three molecules of chlorine or bromine. In this it behaves differently from the derivatives of methane. One atom of carbon cannot be removed from it by oxidation (which it

strongly resists) or otherwise, without the whole molecule falling to pieces. It is, as above mentioned, the simplest member of a series, and its great stability is accounted for by the carbon atoms being united together as a closed ring. The hydrogen atoms are all of equal value, just as they are in methane. Its homologues are derived from it by the substitution of one or more monad hydrocarbon radicals for the same number of hydrogen atoms. However complex these radicals may be they are each one readily oxidised to the group carboxyl (CO.OH) by reagents which have no effect on the benzene nucleus. We thus may distinguish readily between mono-, di-, and tri-derivatives, as indicated already when treating of metamerism.

Naphthalene, $C_{10}H_8$, is another hydrocarbon which may be regarded as formed from the union of two benzene rings—

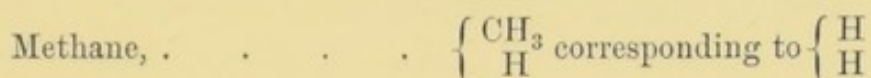


Into the derivatives of benzene we do not propose to enter further till we have studied the derivatives of methane and its homologues, which we term the fatty series.

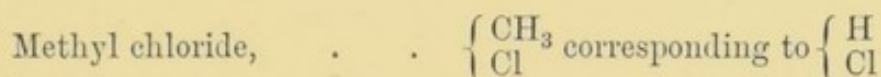
One of the historical theories which in its day has done much for the progress of organic chemistry is Gerhard's *Theory of Types*. We have said above

that we may compare the hydrocarbons to the metals, and in the same way we may compare most of the other classes to other inorganic compounds. Gerhardt referred almost all substances to four typical molecules, viz., those of (1) hydrogen, (2) hydrochloric acid, (3) water, (4) ammonia.

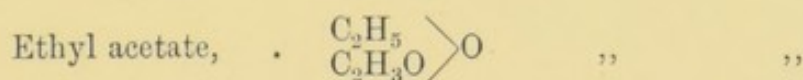
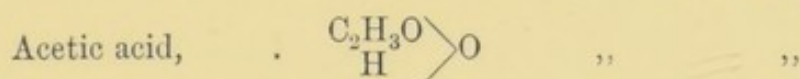
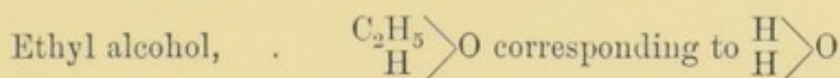
The hydrocarbons were constructed on the first type—



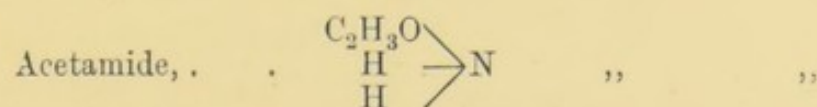
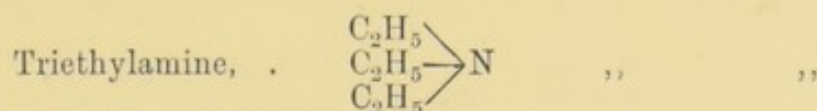
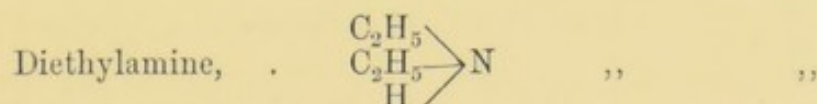
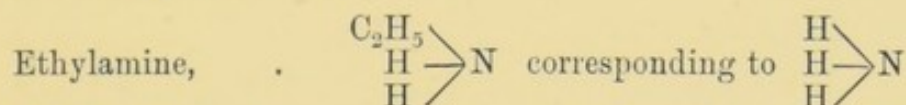
The monohaloid derivatives were constructed on the second, as



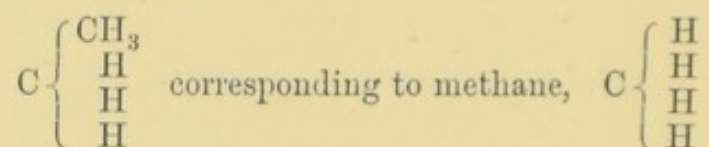
Alcohols and acids, and the compound ethers, on the type of water—



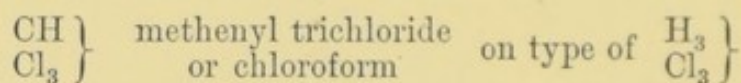
The amines and amides were said to be on the ammonia type, as



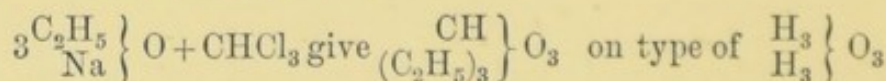
Kekulé added a fifth type, that of methane; and many substances which had been regarded as formed on some of the previous types might be regarded more conveniently as derived from methane, as ethane, which was regarded as $\left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \right\}$, derived from hydrogen, $\left\{ \begin{array}{c} \text{H} \\ \text{H} \end{array} \right\}$, could be regarded as CH_4 , in which one hydrogen was replaced by (CH_3) . Thus—



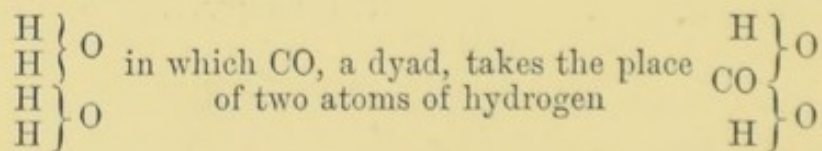
To include many other bodies which could hardly be considered as constructed on these types, Williamson introduced condensed types, as—



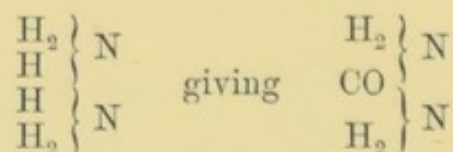
and from chloroform and sodium ethylate, which is a body on the simple water type, we obtain a body having the formula $\text{CH}(\text{C}_2\text{H}_5\text{O})_3$ —



Carbonic acid, H_2CO_3 , is constructed on the double water type—

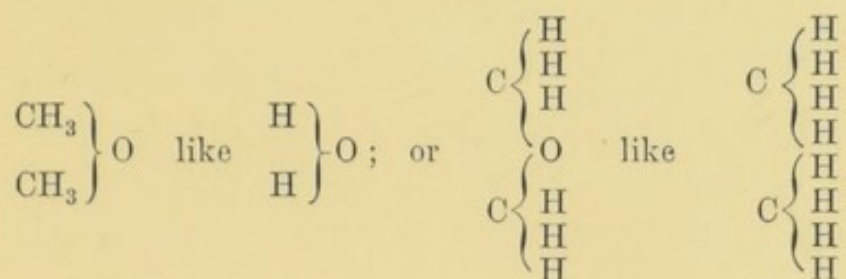


It gives rise to an amide on the double ammonia type—



which is urea or carbamide.

The case of methyl ether can be referred to a double methane type as well as to the water type—

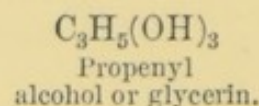
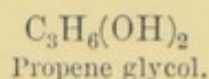
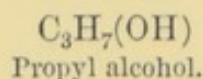


We thus see how types could be used for indicating to some extent the structure of compound bodies which were looked upon as being derived from several simple inorganic bodies by the introduction of what were termed “radicals” for one or more atoms of hydrogen. By the term “compound radical” we mean a group of elements which keeps its entirety throughout a series of compounds, and can be transferred from one to another in chemical reactions just as an element may, but it is by no means necessary that it should be capable of isolation or exist as a real proximate constituent of the members of such a series of substances; in fact, the greater proportion are, as far as we know, incapable of existing singly in the free state.

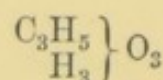
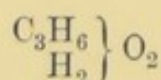
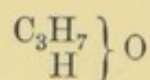
In our modern theory we simply go a step further back, and instead of regarding the compounds as being made up of proximate parts called radicals, we regard them as being formed of atoms only, and if we can find out how the atoms are related to one another, we are far in advance of the theory of types.

The second class of organic bodies, and one of the most important, is that of the alcohols, which we may consider as formed by the replacement of so many

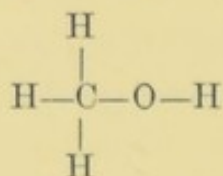
hydrogen atoms in a hydrocarbon, by an equal number of "water residues" or hydroxyl radicals, (HO), as



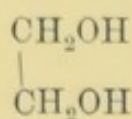
derived from propane C_3H_8 by replacing 1, 2, and 3 atoms of hydrogen by (OH), $(\text{OH})_2$, and $(\text{OH})_3$, and all may be represented on the water type, simple or condensed—



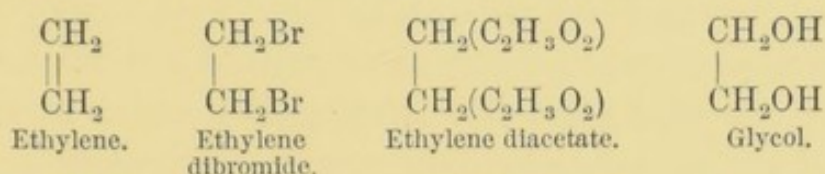
We have three classes of the first kind, or monatomic alcohol as it is often termed, *i.e.*, in which we have only one hydroxyl group, these are termed primary, secondary, and tertiary. Our simplest alcohol is that derived from marsh-gas or methane, viz., methyl alcohol, and as from methane we may consider all our paraffins derived, whether normal, iso, or neo-, by the replacement of 1, 2, 3, or 4 radicals of the type $\text{C}_n\text{H}_{2n+1}$, so may we regard our alcohols as derived from methyl alcohol by the replacement of 1, 2, or 3 radicals of the same type giving rise respectively to primary, secondary, and tertiary alcohols. Methyl alcohol is often termed *carbinol*, and has the structure



Alcohols, however, may contain more than one hydroxyl group, as in glycol, in which we have two—

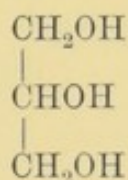


It may be prepared from ethylene by uniting it with bromine, and then converting it into the acetate, and thence into the alcohol. The steps are—



Each alcohol group is a primary one, and can become independently an aldehyde and an acid by oxidation.

From the three carbon hydrocarbons we have glycerin or glycerol—



which is obviously a double primary alcohol and likewise a secondary alcohol, as will be seen on comparing the formula with those below.

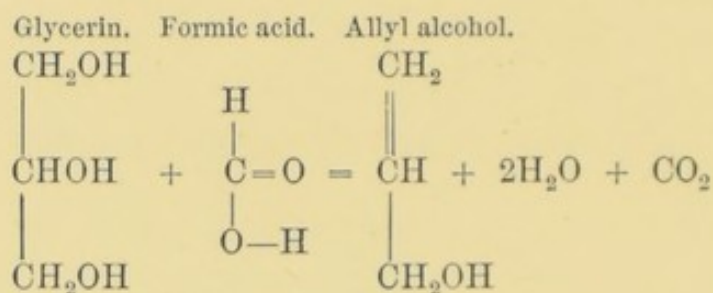
Erythrite is a four hydroxyl, and mannite a six hydroxyl, derivative of the four and of the six carbon paraffin respectively.

The terms monatomic, diatomic, triatomic, tetratomic, and hexatomic alcohols are given respectively to alcohols containing 1, 2, 3, 4, and 6 hydroxyl groups. We have no stable compounds in the state of vapour which contain 2 hydroxyl groups attached to the same carbon atom. For every hydroxyl group therefore we must have an atom of carbon at least. The number of carbon atoms of the original hydrocarbon, which have had a hydrogen atom united to them replaced by hydroxyl, gives the name mono-, di-, tri-, &c., -atomic to the alcohols.

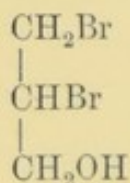
As we have already applied the terms monatomic,

diatomic, &c., to molecules, we shall adopt for alcohols and acids the preferable terms mono-, di-, tri-, hydric, as it is really the hydroxyl groups which we count.

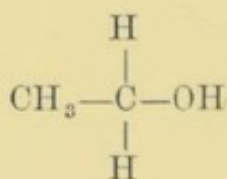
Alcohols may be unsaturated, and such may be regarded as derived from the unsaturated hydrocarbons. One of the best known is allyl alcohol, which may be derived from glycerin by reduction and dehydration—



It, like the olefines, readily combines with bromine directly, forming

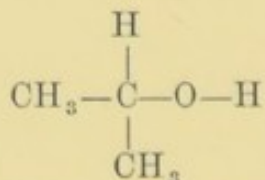


If we replace one of the hydrogens directly united to the carbon in carbinol by a radical, say methyl, CH₃, we get



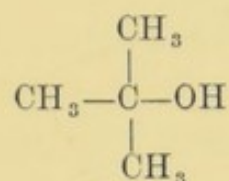
This is then methyl carbinol or ethyl alcohol, C₂H₅—OH.

If two, we get

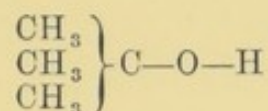


Dimethyl carbinol or isopropyl alcohol, $\left. \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \right\} \text{CHOH}.$

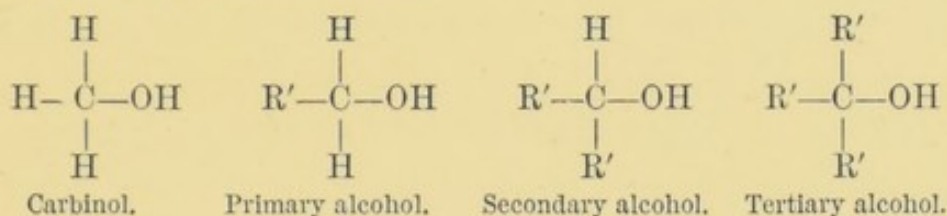
If three,



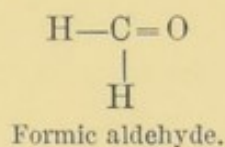
Trimethyl carbinol or tertiary methyl alcohol,



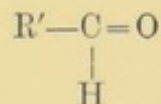
If we look carefully at these we see that we have the following general formulæ—



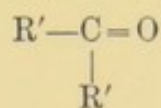
One of the characteristics of a primary alcohol is that it may lose two atoms of hydrogen and become an aldehyde; the simplest aldehyde is



and we get as the general formula of the aldehydes



If we oxidise a secondary alcohol it is still possible to remove two atoms of hydrogen, and we get a ketone or secondary aldehyde having the general formula—

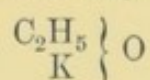


but it is impossible from a tertiary alcohol to produce a substance of aldehydic nature containing the same number of carbon atoms.

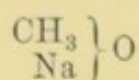
The alcohols and the aldehydes show clearly how we can detect the difference between oxygen united to carbon alone and oxygen united to carbon and to hydrogen. If we treat ethyl alcohol, C_2H_6O , with phosphorus pentachloride, we obtain ethyl chloride, C_2H_5Cl , where evidently the alcohol has lost an atom of hydrogen and one of oxygen, and one atom of chlorine alone has taken their place, that is to say, the amount equivalent to the difference of their valencies. In the case of aldehyde, however, from C_2H_4O we get $C_2H_4Cl_2$; for our one atom of oxygen alone we get two atoms of chlorine, which, being monads, must be united to the carbon only, since the hydrogen is incapable of being at the same time united to both carbon and chlorine, hence we conclude that the oxygen must have been united to the carbon alone.

The alcohols readily exchange one hydrogen atom for an atom of sodium or potassium, giving substances known as sodium or potassium alcohols; or, better, by indicating the radical by the name potassium *alkylate*, as—

Potassium ethylate.



Sodium methylate.

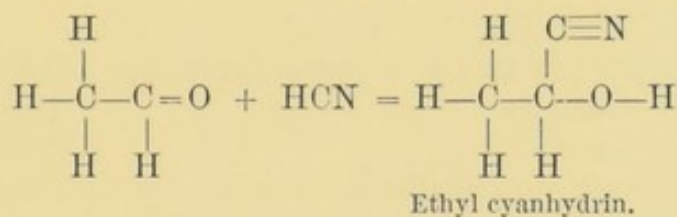
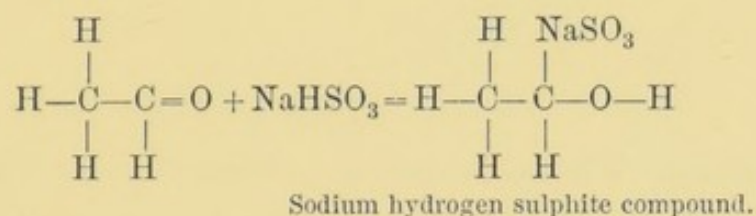
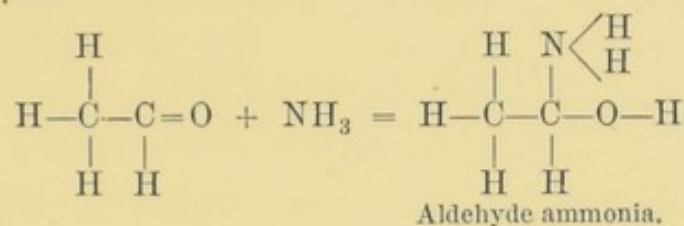


The alcohols readily react with acids to form ethers (ethereal salts) and water.

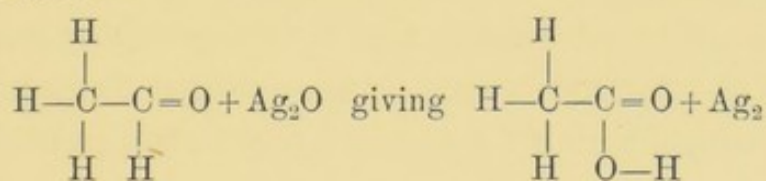
The most conspicuous property of the aldehydes is their tendency to behave more or less as unsaturated bodies, and to combine with oxygen to form acids. They also readily unite with ammonia to form aldehyde

ammonias, with sodium hydrogen sulphite to form a definite crystalline compound, and with hydrocyanic acid to form cyanhydrins.

We will take ethyl aldehyde, $(\text{CH}_3.\text{CHO})$, as an example :—



With oxygen it forms an acid, ethyl aldehyde forming acetic acid—



It is evident that the ketones, or secondary aldehydes, cannot form acids after this fashion, and what we find is, that although they unite with sodium hydrogen sulphite and hydrocyanic acid they do not tend to combine with oxygen, and if treated with an oxidising mixture they break up into substances containing a smaller number of carbon atoms.

We can now see clearly the relation between the alcohol, the aldehyde, and the acid.

	Alcohol.	Aldehyde.	Acid.
Primary, .	$\begin{array}{c} \text{H} \\ \\ \text{R}'-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R}'-\text{C}=\text{O} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R}'-\text{C}=\text{O} \\ \\ \text{O}-\text{H} \end{array}$
Secondary,	$\begin{array}{c} \text{H} \\ \\ \text{R}'-\text{C}-\text{O}-\text{H} \\ \\ \text{R}' \end{array}$	$\begin{array}{c} \text{R}'-\text{C}=\text{O} \\ \\ \text{R}' \end{array}$	None
Tertiary, .	$\begin{array}{c} \text{R}' \\ \\ \text{R}'-\text{C}-\text{O}-\text{H} \\ \\ \text{R}' \end{array}$	None	None

Every primary alcohol contains the group,	(CH ₂ OH)'
„ secondary „ „	(CHOH)''
„ tertiary „ „	(COH)'''
„ aldehyde contains the group, . .	(CHO)'
„ ketone „ „	(CO)''
„ acid „ „	(CO.OH)'

The monobasic acids were on the type theory considered as derived from water by the replacement of one of the hydrogen atoms by an oxidised radical, just as the alcohols were by a purely hydrocarbon radical—

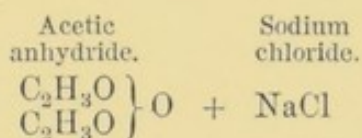
Ethyl alcohol.	Acetic acid.	Water.
$\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{H} \end{array} \} \text{O}$	$\begin{array}{c} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{array} \} \text{O}$	$\begin{array}{c} \text{H} \\ \text{H} \end{array} \} \text{O}$

The aldehydes were then considered as of the hydrogen type—

Ethane.	Ethyllic aldehyde.	
$\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{H} \end{array} \}$	$\begin{array}{c} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{array} \}$	$\begin{array}{c} \text{H} \\ \text{H} \end{array} \}$
Ethyl hydride.	Acetyl hydride.	Hydrogen hydride.

From the simplest monobasic acids we have several derivatives of interest. First, the acid chlorides or chlor-anhydrides, obtained by acting on the acid with phosphorus pentachloride; acetic acid, $\text{CH}_3\text{CO.OH}$, gives acetyl chloride, CH_3COCl , the hydroxyl being replaced by an atom of chlorine.

By acting on an acetate such as that of sodium, with acetyl chloride, the anhydride is obtained. CH_3COCl (acetyl chloride) and CH_3COONa (sodium acetate) give—



Before we consider the various groups of acids, we will more fully explain the differences between the various constitutional formulæ and the empirical one.

An analysis of acetic acid by combustion gave the following results:—

·363 grams of acetic acid gave ·5324 grams of carbon dioxide and ·2178 of water

$$\frac{\text{C}}{\text{CO}_2} = \frac{12}{44} = \frac{3}{11} \quad \cdot 5324 \times \frac{3}{11} = \cdot 1452 \text{ of carbon.}$$

$$\frac{\text{H}_2}{\text{H}_2\text{O}} = \frac{2}{18} = \frac{1}{9} \quad \cdot 2178 \times \frac{1}{9} = \cdot 0242 \text{ of hydrogen.}$$

$$\cdot 1694 = \text{carbon} + \text{hydrogen.}$$

$$\cdot 363 - \cdot 1694 = \cdot 1936 = \text{oxygen by difference.}$$

$$\frac{1452}{12} = 121 \text{ atoms of carbon.}$$

$$\frac{242}{1} = 242 \text{ atoms of hydrogen,}$$

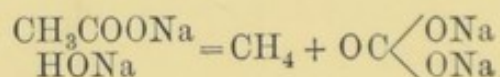
$$\frac{1936}{16} = 121 \text{ atoms of oxygen,}$$

which are in the ratio of 1:2:1.
and the simplest formula is therefore CH_2O .

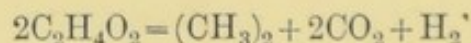
Its vapour density, at a temperature sufficiently above

its boiling-point, is thirty times that of hydrogen at the same temperature and pressure. Its molecular weight is therefore 60, and its empirical molecular formula, $C_2H_4O_2$.

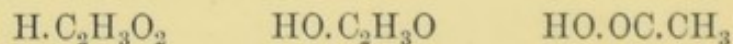
When treated with sodium hydrate, only one of its hydrogen atoms is exchanged for a metal giving rise to $C_2H_3O_2Na$, showing that one hydrogen is different in function from the other three, hence we may write it $H.C_2H_3O_2$. If we act on the acid with phosphorus pentachloride, we lose a hydrogen and an oxygen atom, and in their place have only one chlorine atom, we therefore prove that one hydrogen atom is united to an oxygen atom, so we may write it $C_2H_3O.OH$. If we heat the sodium salt with sodium hydrate, we get one carbon atom with nothing but hydrogen, whilst the other takes all the oxygen, thus:—



hence, we may write it as CH_3COOH . This is also shown by electrolysis, when we get

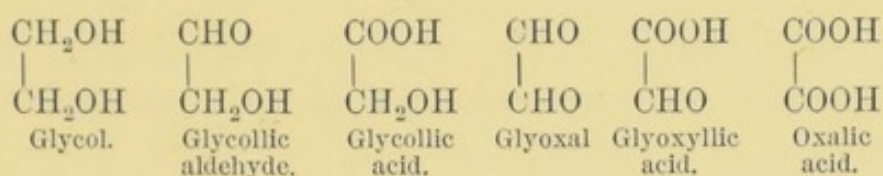


so that the various steps in the building up of our formula are

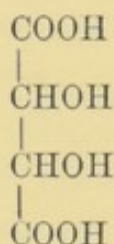


In a primary alcohol we have the hydroxyl united to a carbon atom which has also two hydrogen atoms, and in an acid we have one oxygen atom instead of these two hydrogen atoms. Now it is possible to have an acid possessing alcoholic as well as acid qualities. The simplest is that derived from glycol, which, as we have already seen, consists of two primary alcohol groups,

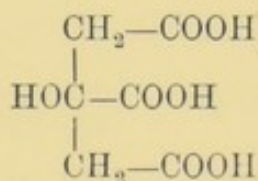
which can each become aldehyde groups, and these in turn become carboxyl groups, so we may have the following six distinct substances formed by the oxidation of glycol :—



As the carboxyl group is the characteristic acid group, and it is the hydrogen in it which is replaceable by a metal, the basicity of the acid depends on the number of carboxyl groups it contains, but the total number of hydroxyl groups indicates its atomicity or hydricity. We say that tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, is a tetrahydric, but a dibasic acid. Its constitutional formula is—



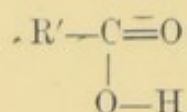
Citric acid is tetrahydric and tribasic—



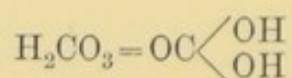
We thus see how we may classify the acids into series, first from the series of hydrocarbons from which they are derived, and then from the radicals and the number of them which have been substituted into the paraffins.

The first series is the monobasic and monohydric

series known as the fatty acids, which have the general formula—



or empirically, $\text{C}_n\text{H}_{2n}\text{O}_2$, as acetic acid, $\text{C}_2\text{H}_4\text{O}_2$. The second series is monobasic and dihydric, of which the first member is carbonic acid—



which behaves in many ways as a dibasic acid, because there is no difference between the two hydroxyls, both being united to the same carbon atom, which is at the same time attached to an oxygen atom. Its *neutral* salts are like sodium hydrogen carbonate, NaHCO_3 , in which we have it acting as a monobasic acid. It may be called oxyformic acid, as glycollic acid is oxyacetic, and lactic acid is oxypropionic, an oxyacid being one in which hydroxyl is replaced for hydrogen in the original acid. In lactic acid, just as in carbonic acid, we may have sodium replacing the hydrogen of the hydroxyl, not in the acid, but in the alcoholic group, by using metallic sodium, which we saw reacted with alcohols as with water, and we get the sodium salt of sodium-lactic acid—

Ethy- lidene.	Ethylidene lactic acid. (ordinary).	Ethylene.	Ethylene lactic acid.	Sodium lactate.	Disodium lactate.
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH} \\ \diagdown \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CHOH} \\ \\ \text{CO.OH} \end{array}$	$\begin{array}{c} \text{CH}_2- \\ \\ \text{CH}_2- \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CO.OH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CHOH} \\ \\ \text{CO.ONa} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CHONa} \\ \\ \text{CO.ONa} \end{array}$

The dibasic acids may be regarded as formed from the glycols, and have the general formula $\text{C}_n\text{H}_{2n}(\text{CO.OH})_2$,

the simplest being oxalic acid, which is dicarboxyl. The other important members of this series are succinic, isosuccinic, and pyrotartaric acids.

The most interesting dibasic and trihydric acid is malic acid, the acid in many fruits; and of dibasic and tetrahydric acids, tartaric acid and its modifications are the most important.

The ethers are compounds of hydrocarbon radicals with electro-negative elements or groups of elements, and correspond exactly to salts as previously defined. We are more logical, however, here, since we make no exception of oxygen, but rather the reverse, for the oxygen ethers are ethers *par excellence*.

When the electro-negative radical is an element we call the ether *simple*, and when it is a group of elements the ether is said to be *compound*, as

Simple ethers—

Ethyl chloride.
 $\text{C}_2\text{H}_5\text{Cl}$

Ethyl oxide or ether.
 $(\text{C}_2\text{H}_5)_2\text{O}$

Compound ethers—

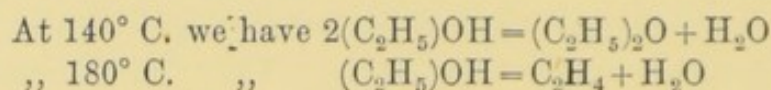
Ethyl nitrate.
 $\text{C}_2\text{H}_5\text{NO}_3$

Ethyl sulphate.
 $(\text{C}_2\text{H}_5)_2\text{SO}_4$

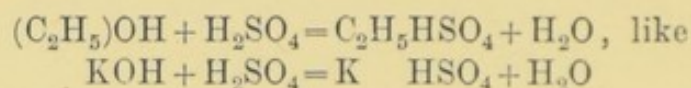
Ethyl hydrogen sulphate.
 $(\text{C}_2\text{H}_5)\text{HSO}_4$

Into the various modes of producing the very numerous ethers we cannot enter here, but will study some very interesting cases of metamerism which some members present, and the transformations of which indicate very clearly the modes of deducing rational formulæ from the reactions of the substances. Before taking special cases, however, we must first consider the general process of making oxygen ethers known as the “continuous etherification process.” Ordinary (ethyl) alcohol

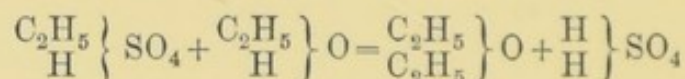
is converted into ethyl ether by the action on it of sulphuric acid. It was formerly supposed to be simply a case of dehydration, and that if the temperature were higher this dehydration would be more complete, as we may judge from its products—



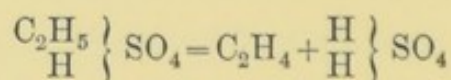
The classical researches of Williamson proved conclusively that it was not a case of simple dehydration, but that first we have an ether formed by the interaction of the sulphuric acid and the alcohol—



and that this ether (known as ethyl hydrogen sulphate, or sulphovinic acid, which has been isolated, and which acts as a monobasic acid) is decomposed by another molecule of alcohol into the oxygen ether and sulphuric acid again—



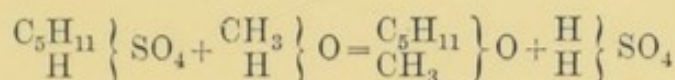
If the temperature be high, the ethyl sulphuric acid decomposes into ethylene and sulphuric acid—



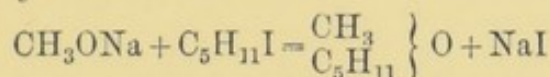
If we use a mixture of alcohols instead of one, we ought to obtain *mixed ethers*, that is, ethers which may be considered as water with its hydrogen atoms replaced by different radicals. If the older theory were correct, we ought to obtain a *mixture of ethers*.

By taking amyl alcohol $\text{C}_5\text{H}_{11}\text{OH}$ and heating it with sulphuric acid so as to form the amyl hydrogen sulphate,

and then adding methyl alcohol, amyl methyl oxide was obtained, thus—

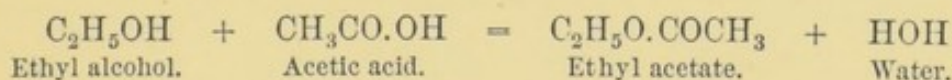


Amyl methyl ether boils at 92°C ., but methyl ether, $\text{CH}_3 \left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \right\} \text{O}$, boils at -21°C ., being a gas at ordinary temperature, and amyl ether, $\text{C}_5\text{H}_{11} \left\{ \begin{array}{l} \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{array} \right\} \text{O}$, boils at 176°C ., so that we have no doubt as to the product of the reaction, which may also be prepared by acting on sodium methylate with amyl iodide—



Thus prepared it is found to be identical in every respect with that obtained by the former process.

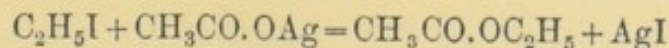
The chief process employed in the preparation of the ethers is the reaction between the alcohol and the corresponding acid in presence of a dehydrating agent, since water causes a reverse change, as



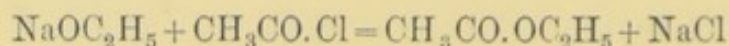
If, however, we heat ethyl acetate with water, we obtain ethyl alcohol and acetic acid—



To prevent this reaction a dehydrating agent must be present. We may use the haloid ether and cause it to react on the silver salt of the acid of which we require the ether. To obtain ethyl acetate thus, we would use ethyl iodide and silver acetate—



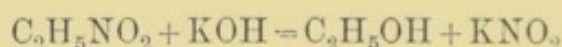
or an analogous method is to use sodium ethylate and acetyl chloride—



If we endeavour to prepare ethyl nitrite by the action of nitrous acid upon ethyl alcohol, we obtain a very volatile liquid, boiling at 12°C . By using the other reaction, and acting on silver nitrite with ethyl iodide, we obtain a totally different body which boils at 113°C . Which, then, is the true nitrite?

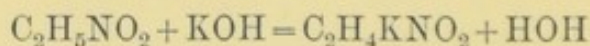
The action of water, or, better, of alkalies, splits up the ethereal salts into the alcohol and acid from which they are derived.

The first-mentioned liquid, boiling at 12°C ., when acted upon by potassium hydrate, gives ethyl alcohol and potassium nitrite—



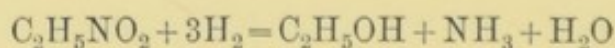
This is, therefore, the true ethyl nitrite.

The second, known as nitro-ethane, when similarly treated gives rise to a metallic derivative—

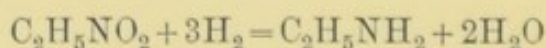


Their molecular structure, however, is best seen by considering the action of reducing agents upon each.

Ethyl nitrite, when treated with nascent hydrogen, yields ethyl alcohol, ammonia, and water—

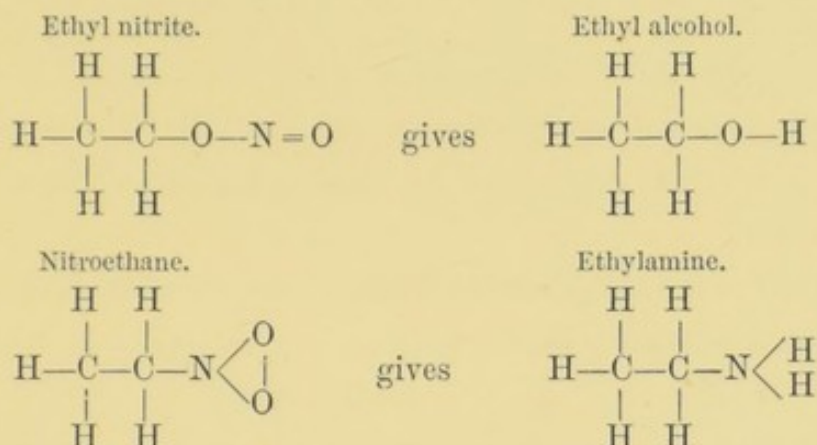


Nitro-ethane, when similarly treated, gives ethylamine and water—

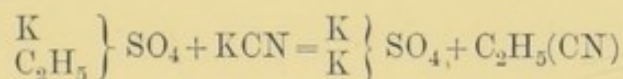


The conclusions to be drawn are, therefore, that in the

nitrite the nitrogen is attached to the radical by means of an oxygen atom, but that in the nitro-body the nitrogen is directly united to the radical. Thus—



We have likewise two substances having the empirical formula $\text{C}_3\text{H}_5\text{N}$, but their formation from ethyl compounds justifies us in writing $\text{C}_2\text{H}_5(\text{CN})$. One is prepared from potassium ethyl sulphate and potassium cyanide—



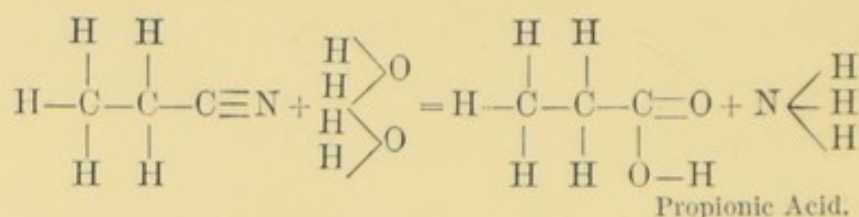
This cyanide boils at 98°C ., and has a smell which is not unpleasant. It is called ethyl cyanide or propionitrile.

If ethyl iodide be heated with silver cyanide, we obtain a compound of the same composition as the last—



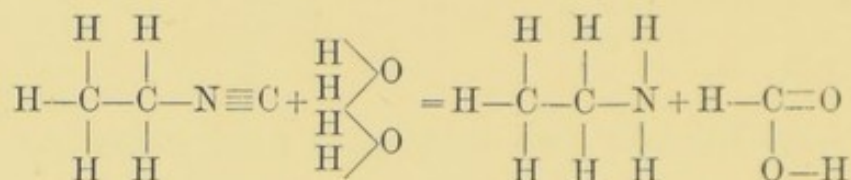
It however boils at 82°C ., and has an indescribably disgusting odour, which produces violent headaches even in minute quantity. It is called ethyl isocyanide or carbamine.

Ethyl cyanide reacts with water (in presence of bases especially), thus—



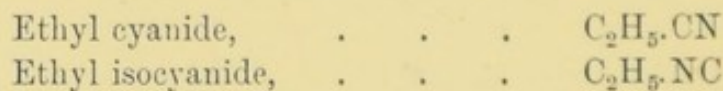
The nitriles or true cyanides react with water to give an acid containing the same number of carbon atoms, and give the nitrogen as the simplest amine, *i.e.*, ammonia.

Ethyl isocyanide or carbamine reacts with water (in presence of acids), thus—

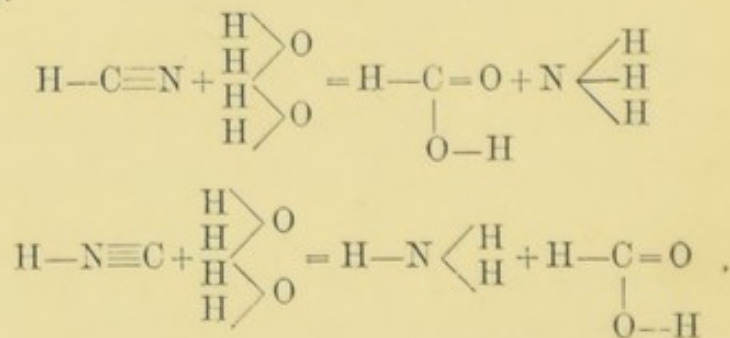


The isocyanides react with water to form an amine with an atom of carbon less than the isocyanide contains, and the simplest acid of the fatty series, *i.e.*, formic acid.

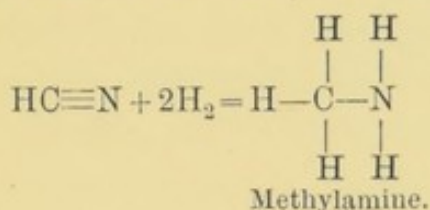
Their formulæ may therefore be written thus—



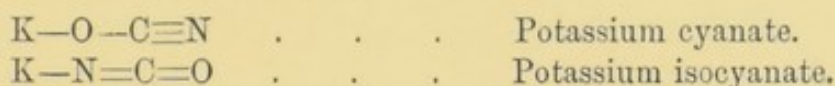
The two series unite in hydrocyanic or prussic acid, the simplest member of the series, whose radical is hydrogen. The products of its reaction with water are formic acid and ammonia. It therefore agrees with the reactions of either.



It has an unpleasant smell and is very poisonous, like the isocyanides, and, like them, combines directly with hydrochloric acid. It unites with nascent hydrogen to form the amine with the same number of carbon atoms, which is a characteristic of the true cyanides.

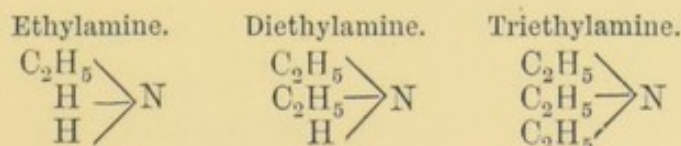


We similarly have cyanates and isocyanates, thiocyanates and isothiocyanates. Of the first member, cyanic acid, we have an isomer, isocyanic acid, and the potassium salts of both are known.



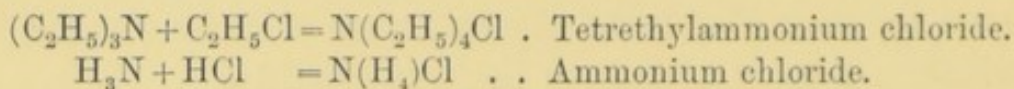
The first is formed by passing cyanogen chloride into potassium hydrate solution. The second is formed by fusing potassium cyanide with lead oxide, and is ordinary potassium cyanate.

The amines are compound ammonias, that is, substances having the general properties of ammonia, and which may be regarded as ammonia with 1, 2, or 3 monad alcohol radicals for the same number of its hydrogen atoms. They are called respectively primary, secondary, and tertiary amines. Taking ethyl as a typical radical, we have—



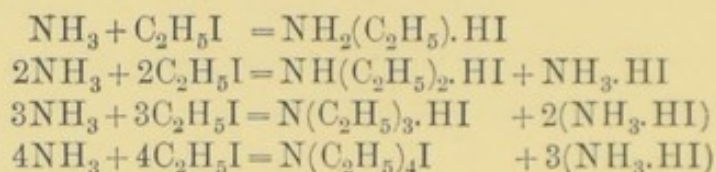
All are strongly basic bodies, and unite directly with acids to form salts like those of ammonium. They like-

wise unite with haloid ethers, so that we obtain bodies of the type of ammonium chloride in which each hydrogen atom is replaced by an alcohol radical.



When heated these compounds break up into the two molecules from which they were derived, at least when the alcohol radicals are all the same.

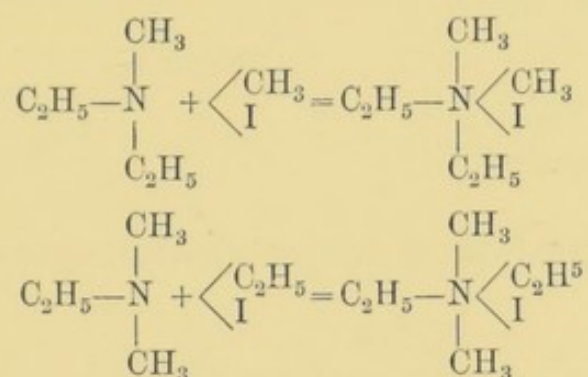
All are obtained simultaneously by the action of ammonia on the corresponding haloid ether. The same proportions are required for each :—



For details as to their separation, works on organic chemistry must be consulted. Here we will only remark that on boiling with an alkali we may distil over the mono-, di-, and tri-ethylamines, but the tetrethyl ammonium iodide is not decomposed ; it is, however, insoluble in strong alkaline solutions and may thus be separated. If it be treated with moist silver oxide the iodine may be replaced by hydroxyl, and $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$ obtained as a solid body, having the general caustic and other properties of potassium hydrate.

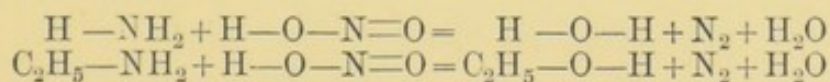
The tetrammonium compounds are very interesting, because of the light they throw upon the constitution of ammonium salts. Nitrogen and chlorine do not combine directly, and, when they are combined, tend to separate with explosive violence. It was therefore argued that we ought not to represent the chlorine in ammonium chloride as directly united to the nitrogen, because,

when we add hydrochloric acid to ammonia, such a representation would mean that the chlorine must leave the hydrogen with which it combines readily to combine with the nitrogen. If, however, we mix methyl diethylamine with methyl iodide they unite to form dimethyl diethyl ammonium iodide, which may also be formed by combining dimethyl ethylamine with ethyl iodide, and then is found to possess exactly the same properties.

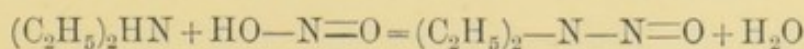


Hence, we see that we have a true compound formed and not a "molecular compound," for these two bodies should then split up by heating into the two molecules which formed them, and thus behave differently from one another; they both, however, give methyl diethylamine and methyl iodide. Nitrogen is therefore pentad in the ammonium salts.

The action of nitrous acid on the primary amines is similar to that on ammonia—

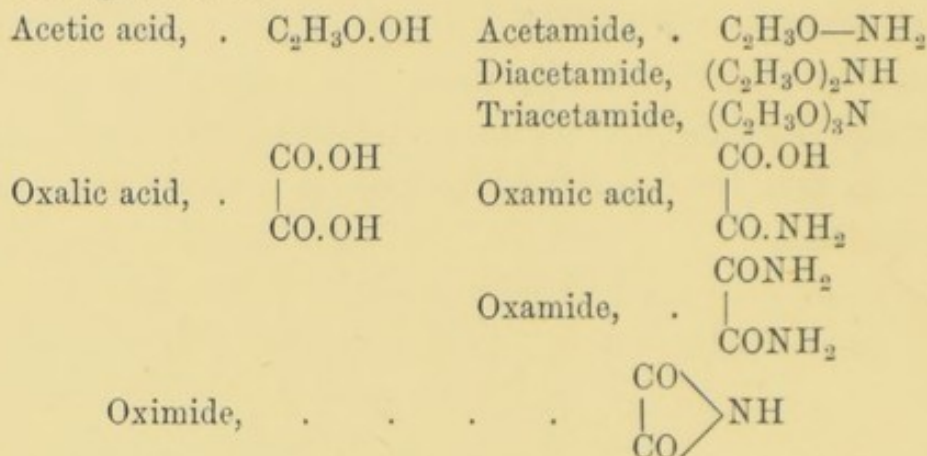


On the secondary it behaves otherwise, diethylamine yielding diethyl nitrosamine—

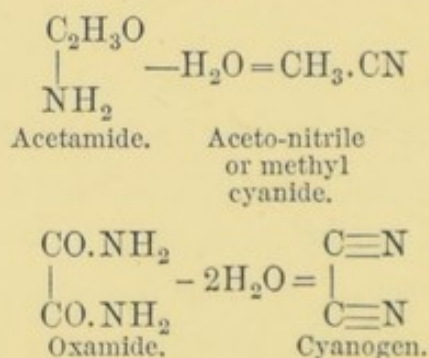


It has no action on the tertiary amines.

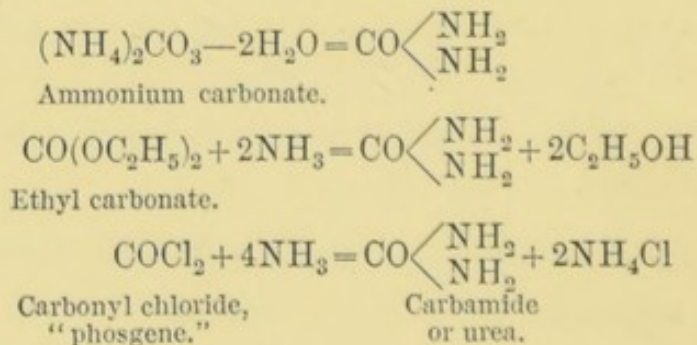
The amides are related to the acids as the amines are to the alcohols—that is, one hydroxyl, (OH), is replaced by amidogen, (NH₂), or two by imidogen, (NH), or three by nitrogen alone—



By dehydration of the amides the cyanides are obtained—



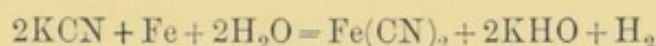
The amides themselves are obtained by dehydration of the ammonium salts, or by the action of ammonia on one of the ethers corresponding, or upon the acid chloride—



Reference has been made above to several bodies containing cyanogen; several others containing the same radical present points of great interest.

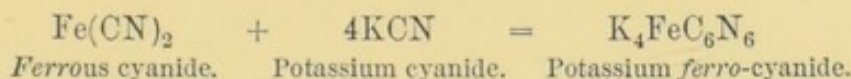
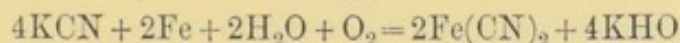
One of the most interesting is the common substance, potassium ferrocyanide. It is prepared on a large scale by heating together in iron vessels, scrap iron, potassium salts and nitrogenous organic matter. These react to produce potassium cyanide. The potassium cyanide formed dissolves the iron in presence of air and water, forming ferrous cyanide and potassium hydrate. The ferrous cyanide combines with excess of potassium cyanide to form the ferrocyanide—

Ferrous cyanide.

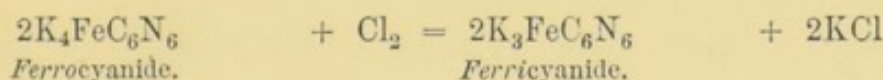
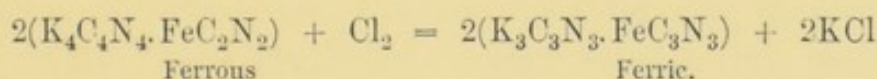


If air be present—

Air.

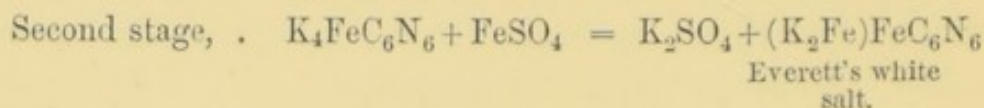
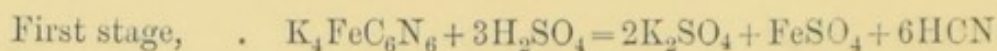


Oxidising agents convert the ferrous into the ferric cyanide, and we obtain the *ferricyanide*.

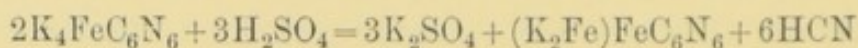


Potassium ferricyanide is a useful oxidising agent in alkaline solution.

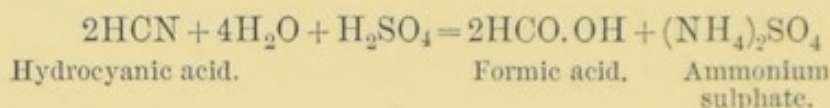
The action of sulphuric acid upon potassium ferrocyanide is an interesting one. If dilute we may represent the action thus—



or as one—



If the sulphuric acid be strong, a small quantity only of water being present, we have carbon monoxide produced along with ammonium sulphate, from the decomposition of the hydrocyanic acid, thus, as we saw with the ethereal cyanides—



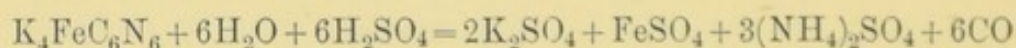
The formic acid is, however, dehydrated by the strong sulphuric acid giving carbon monoxide—



So we may write the reaction thus—

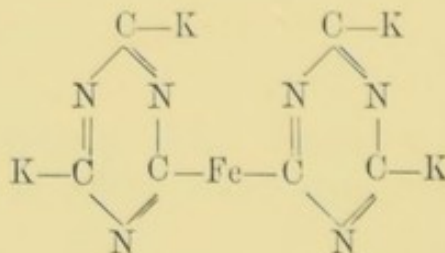


and the entire equation from the ferrocyanide—



The water required is derived from the water of crystallisation of the ferrocyanide and from what is always present in ordinary strong sulphuric acid, which is approximately $12SO_3 + 13H_2O$ or $12H_2SO_4.H_2O$.

The constitution of potassium ferrocyanide is probably



corresponding as regards its nitrogen and carbon to cyanuric acid.

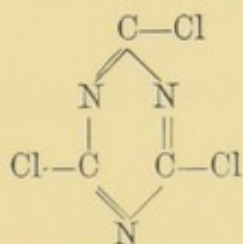
Four polymeric bodies are known with the empirical formula HCNO.

HCNO	.	.	.	Cyanic acid.
(HCNO) ₂	.	.	.	Fulminic acid.
(HCNO) ₃	.	.	.	Cyanuric acid.
(HCNO) _n	.	.	.	Cyamelide.

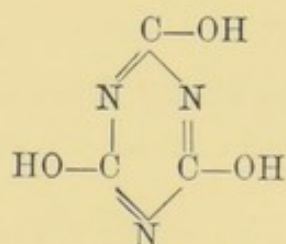
When urea (carbamide) is heated in a current of chlorine gas, or even alone, we obtain cyanuric acid. When this is distilled we obtain cyanic acid, HCNO, which is a very unstable body, and when taken out of the freezing mixture, which is necessary for its condensation, it polymerises with explosive violence, becoming cyamelide, which, like cyanuric acid, passes back to cyanic acid on heating.

Cyanuric acid by the action of phosphorus pentachloride is converted into cyanuric chloride, $C_3N_3Cl_3$, which water reconverts into the acid.

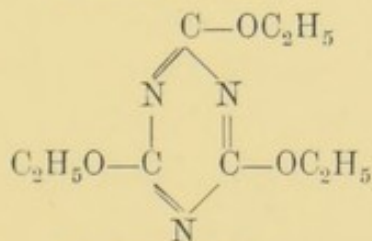
From cyanuric acid we have two isomeric series of ethers, the cyanuric and the isocyanuric. The structure of these substances is probably



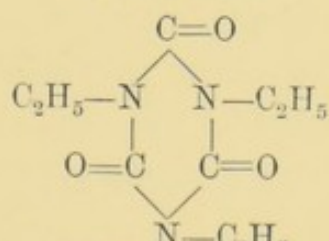
Cyanuric chloride.



Cyanuric acid.

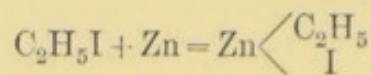


Ethyl cyanurate.

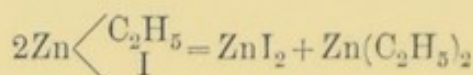


Ethyl isocyanurate.

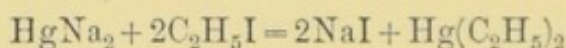
Of the organo-metallic bodies the most important are the compounds of zinc with methyl and ethyl. When zinc filings and ethyl iodide are heated together they combine directly, forming zinc ethyl iodide—



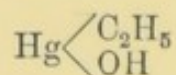
When this solid body is further heated we obtain zinc ethide (zinc ethyl) and zinc iodide—



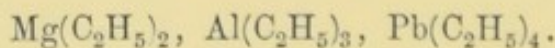
Mercury ethide is prepared by acting on liquid sodium amalgam with ethyl iodide (in presence of ethyl acetate, the function of which is not understood).



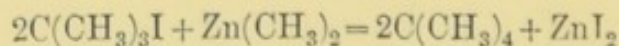
Mercury ethide combines with mercuric chloride to form mercury ethyl chloride, $\text{HgC}_2\text{H}_5\text{Cl}$, which, when treated with moist silver oxide, gives the corresponding hydrate, a powerfully basic body having the formula



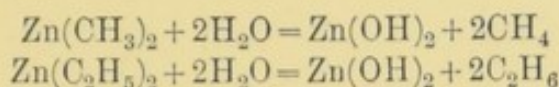
The molecular formulæ of the magnesium, aluminium, and lead ethides are respectively



The very great chemical activity of the zinc compounds makes them invaluable as reagents in replacing the halogens by the alcohol radicals. Tertiary butyl iodide and zinc methide give neopentane and zinc iodide.



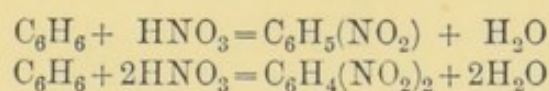
By acting upon them with water we get the paraffins



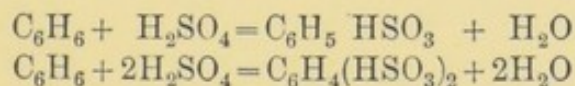
The aromatic compounds are, as above stated, regarded as derivatives of benzene, C_6H_6 . They are characterised by great stability, although so far from complete saturation. A metamer of benzene is known which shows this difference in a striking manner. Di-propargyl, formed by removing from di-allyl tetrabromide four molecules of hydrobromic acid, unites with bromine with great violence to form $\text{C}_6\text{H}_6\text{Br}_8$. (C_3H_5) , allyl, acts as either a monad or triad radical. $(\text{C}_3\text{H}_5)_2$, di-allyl, unites with 2Br_2 to form $\text{C}_6\text{H}_{10}\text{Br}_4$, di-allyl tetrabromide. $\text{C}_6\text{H}_{10}\text{Br}_4 - 4\text{HBr} = \text{C}_6\text{H}_6$, di-propargyl, = hexune.

Benzene unites with bromine only very slowly, and under the influence of direct sunshine, to form as its extreme product $\text{C}_6\text{H}_6\text{Br}_6$.

The most characteristic reactions of the aromatic hydrocarbons are their reactions (1) with nitric acid to form a nitro-body and water, as



(2) With sulphuric acid to form sulphonic acids and water, as

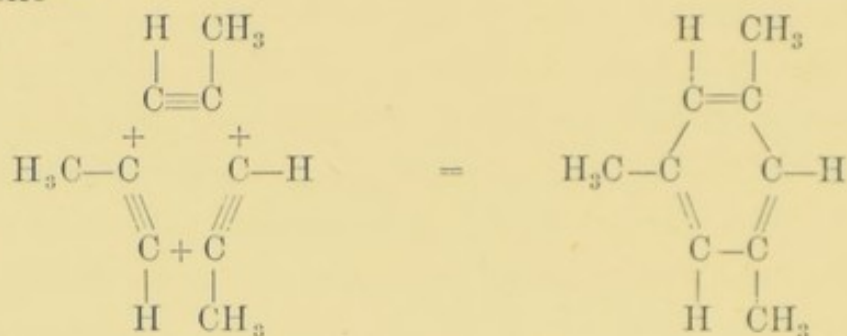


(3) Although we cannot oxidise benzene without destroying it, its homologues (unlike the paraffins) are readily oxidised to benzene-carboxylic acids.

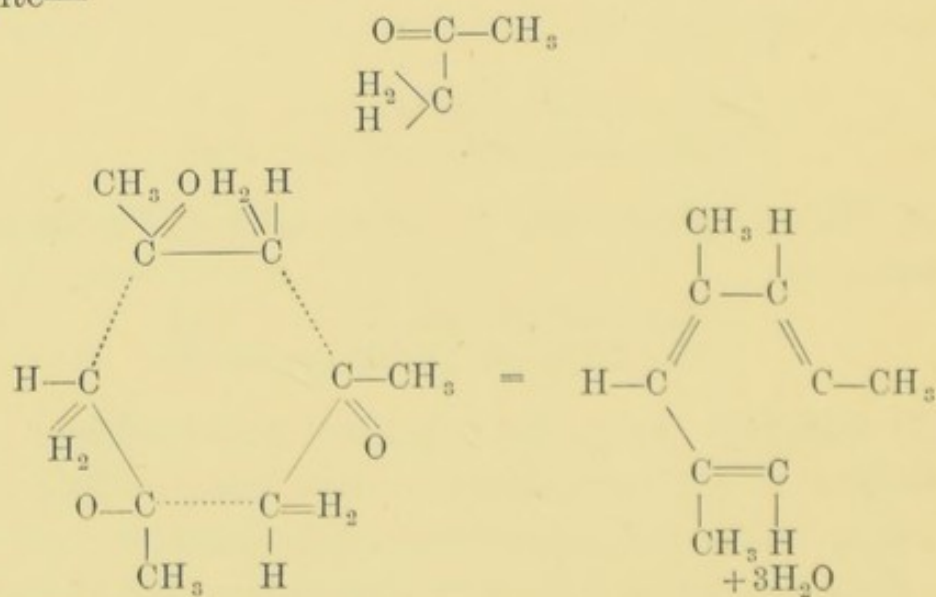
Benzene may be formed by the condensation of acetylene by the action of heat—



In the same way from allylene or methyl acetylene, $\text{C}_3\text{H}_4 = \text{C}_2\text{H}(\text{CH}_3)$, we obtain mesitylene or trimethyl benzene—

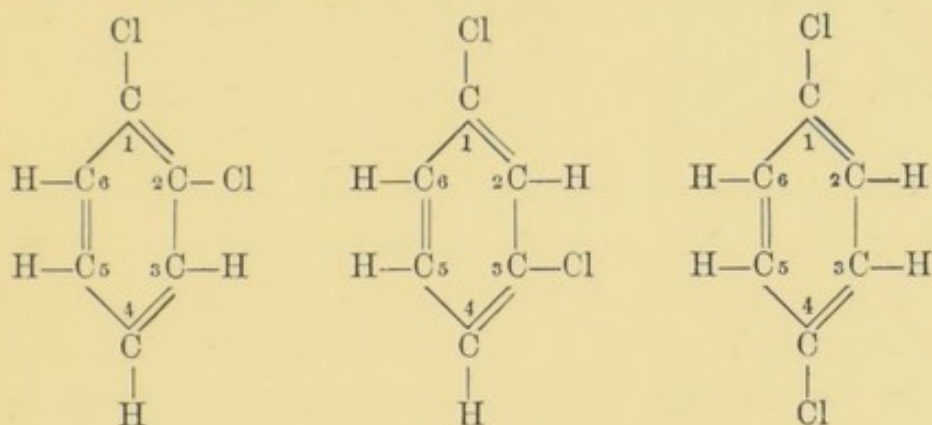


Mesitylene is also formed by the dehydration of acetone, $\text{CH}_3-\text{CO}-\text{CH}_3$, which for our purpose we will write—



As Kekulé's formula indicates, all the hydrogen atoms

are similar in every way. Their value is identical in replacement. We saw this was not the case with the hexanes, where we may have several isomeric monohaloid derivatives from each of them, but only one monochlorobenzene is known. We have, however, three dichlorobenzenes indicated by theory, and three only are known—



which are respectively known as the

1 : 2, or ortho-
 1 : 3, or meta-
 1 : 4, or para-

} dichlorobenzenes.

In the first, the chlorine is on two adjacent carbon atoms; in the second, the chlorine is on two carbon atoms separated by one other atom of carbon; in the third, the chlorine is on two carbon atoms separated by two other atoms of carbon.

How are we able to decide which is the ortho-, the meta-, and the para-modification?

If by further action of chlorine we convert each di-chloro-benzene into tri-chloro-benzenes, of which there are also three, we find that from the ortho-compound we can obtain two, and two only; from the meta-com-

pound we can obtain all three ; but only one is obtained from the para-compound.

That this must be so is apparent from the following. Four hydrogen atoms remain in the di-chloro-benzenes ; an atom of chlorine may replace any one of them, when we will obtain the following four from each :—

Ortho- 1:2.	Meta- 1:3.	Para- 1:4.
(a) 1:2:3	(a) 1:2:3	(b) 1:2:4
(b) 1:2:4	(b) 1:3:4	(b) 1:3:4
(b) 1:2:5	(c) 1:3:5	(b) 1:4:5
(a) 1:2:6	(b) 1:3:6	(b) 1:4:6

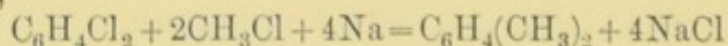
All those marked (a) are alike, for in each we have the chlorine on three adjacent carbon atoms.

In those marked (b) we have it on two together and one separated.

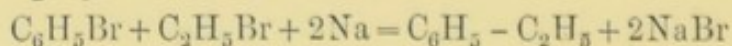
In that marked (c) the carbon atoms are united to chlorine and hydrogen alternately.

By the study of such reactions, properly selected, we can determine the orientation, as it is termed, of the various radicals introduced in place of the original hydrogen atoms.

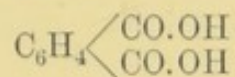
As to the homologues of benzene, we have isomerism and metamerism well illustrated, as mentioned (p. 95). Monomethyl benzene exists as toluene, $C_7H_8 = C_6H_5 - CH_3$, and only one is known ; but of dimethyl benzenes, C_8H_{10} , we know three, corresponding to the three di-chloro-benzenes and from which each one may be produced in turn by the action of sodium and methyl chloride,



We have also metamerism with these, ethyl benzene, $C_6H_5 - C_2H_5$, and prepared from



When oxidised the three dimethyl benzenes give rise to three isomeric dicarboxylic acids—



Ethylbenzene gives mono-carboxyl benzene, or benzoic acid, $\text{C}_6\text{H}_5 - \text{CO.OH}$.

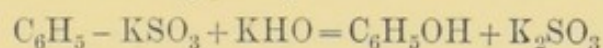
The most interesting reactions of benzene and its homologues are :—

1. Action of chlorine—(a) When hot the chlorine replaces the hydrogen in the side chain. (b) When cold, and in presence of iodine, the chlorine replaces the hydrogen in the benzene nucleus.

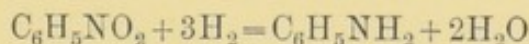
2. Action of strong nitric acid produces nitro-compounds by the replacement of hydrogen by the monad group NO_2 , water being simultaneously produced.

3. Action of strong sulphuric acid to form sulphonic acids and water.

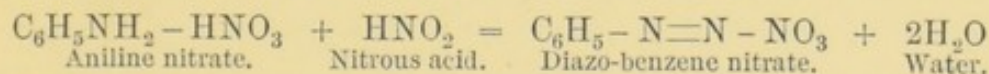
4. By fusion of the sulphonates with potassium hydrate we obtain the hydroxyl derivative and a sulphite—



5. By reduction with nascent hydrogen, or other reducing agent, we may convert the nitro-derivative into the corresponding amido-derivative, as

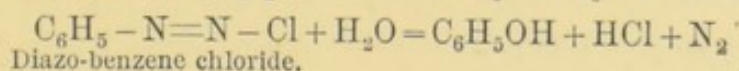


6. The action of nitrous acid on the salts of the amido-derivative gives rise to salts of diazo-compounds—



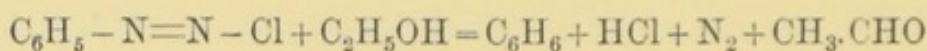
These decompose as follows :—

1. With water they produce the hydroxyl derivatives—

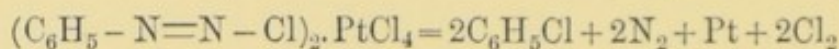


This corresponds to the conversion of a fatty amine into an alcohol by nitrous acid.

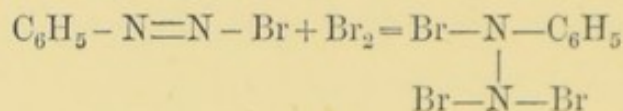
2. With alcohol we get the hydrocarbon itself and aldehyde—



3. The platinochlorides, on distillation with dry sodium carbonate, yield the chlorinated hydrocarbon—



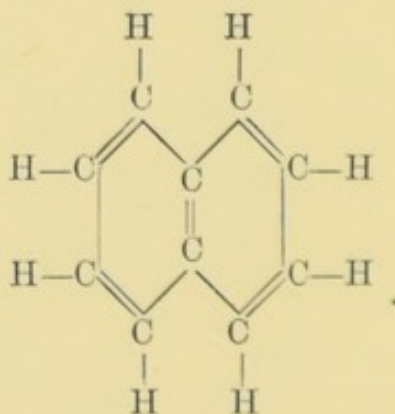
4. The bromides combine with a molecule of bromine—



The tribromide, on dry distillation or boiling with strong alcohol, gives the brominated hydrocarbon—



Another very interesting hydrocarbon, naphthalene, C_{10}H_8 , is obtained also from coal tar, and it is likewise the starting-point of a series. It is like a double benzene nucleus, and is represented thus:—



What reasons have we for supposing this represents the constitution of naphthalene? We have the following, among other proofs:—

1. Naphthalene when oxidised gives phthalic acid $C_6H_4(CO.OH)_2$, which is an ortho-derivative of benzene, that is, the two carboxyl groups occupy the positions 1:2 (see above).

2. We get the same body from the oxidation of dichloronaphthoquinone.

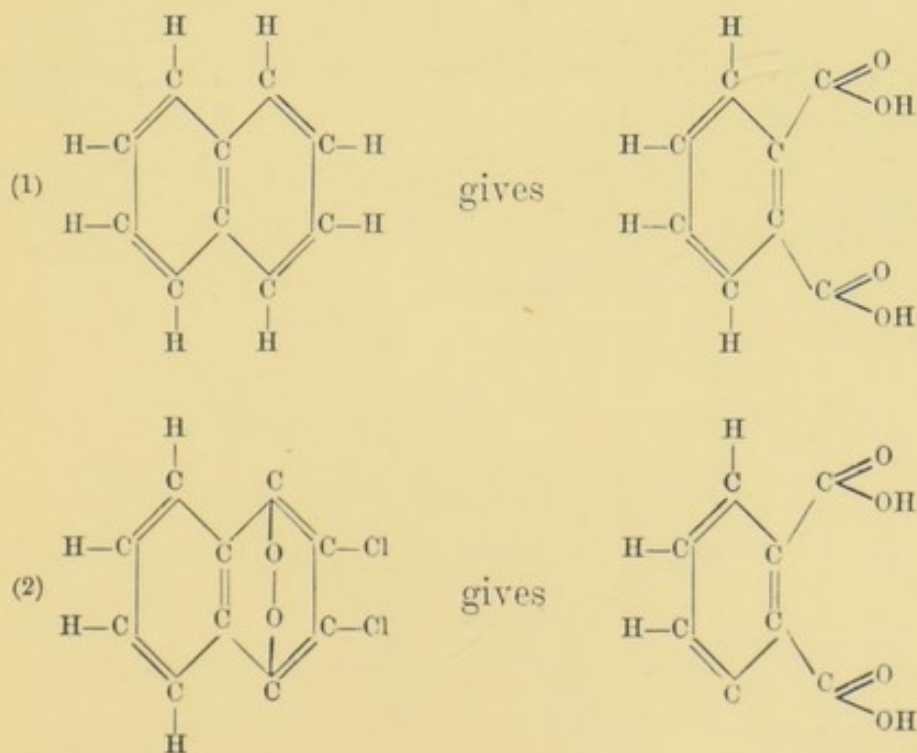
3. If we use, however, pentachloronaphthalene, which is obtained by acting on dichloronaphthoquinone with phosphorus pentachloride, we obtain tetrachlorophthalic acid.

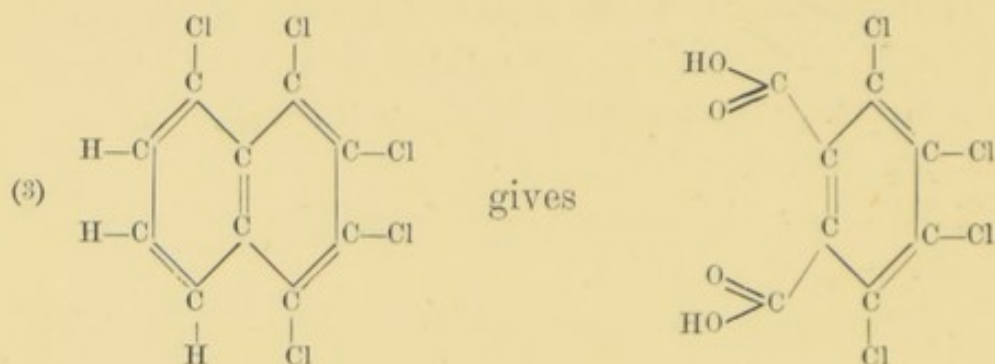
Reaction 1 shows it has one benzene nucleus.

Reaction 2 shows it has one benzene nucleus.

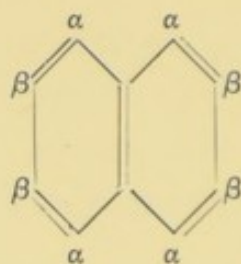
Reaction 3 shows it has two benzene nuclei, because the nucleus in 2, which was then destroyed, has been rendered more stable as regards oxidation, and the other nucleus is destroyed, the nucleus being marked as it were, by the two chlorine atoms.

Graphically we may represent these changes thus:—





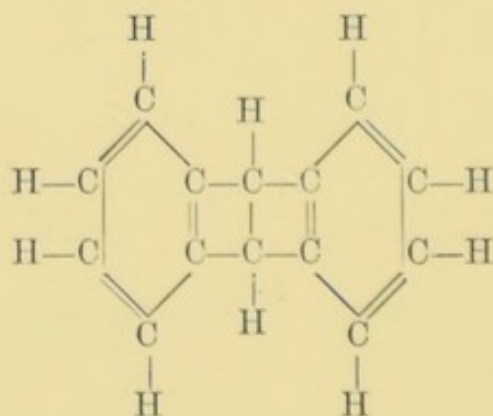
It will readily be seen from the above formula that we ought to have two mono-derivatives of naphthalene. Now two are known, and two only, of each kind, which are known as the α and β derivatives respectively—



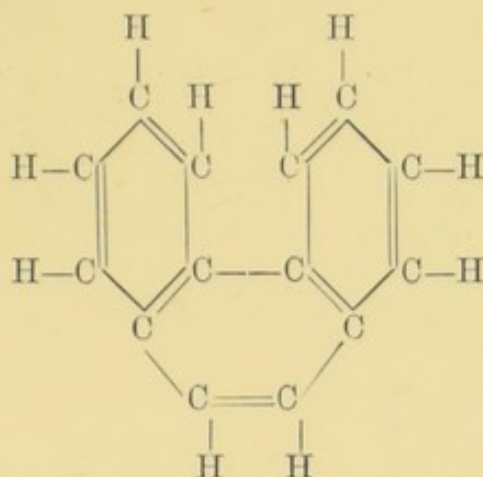
The four α positions are identical, as are also the four β positions.

The constitution of two other important hydrocarbons, anthracene and phenanthrene, may be shown to be—

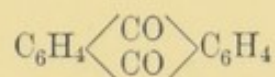
Anthracene.



Phenanthrene.



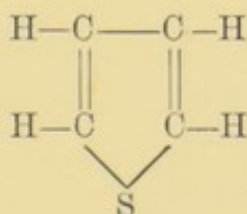
Anthracene on oxidation gives anthraquinone—



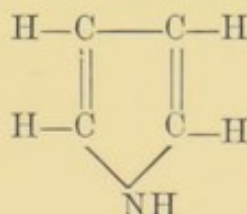
and this on treatment with strong sulphuric acid so as to give the disulphonic acid and subsequent fusion with sodium hydrate, produces the very important colouring matter alizarin, which is one of the di-hydroxy-anthraquinones.

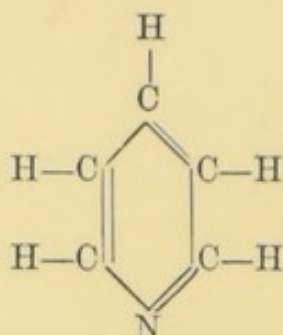
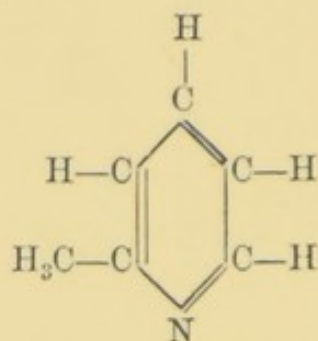
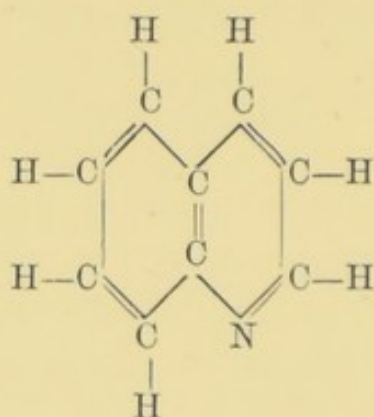
Not only do we have carbon atoms uniting to form a stable nucleus, but we have them uniting with those of other elements also, as the following graphic formulæ of some interesting compounds indicate:—

Thiophene.
 $\text{C}_4\text{H}_4\text{S}$



Pyrrol.
 $\text{C}_4\text{H}_5\text{N}$



Pyridine.
 C_5H_5N  α Picoline.
 C_6H_7N Quinoline.
 C_9H_7N 

Picoline, of which there are three modifications, is metameric with aniline. Unlike aniline it acts as a tertiary base, and is unaffected by nitrous acid, which converts aniline (as it does other primary amines) finally into the hydroxyl derivative, $C_6H_5NH_2$ becoming C_6H_5OH , just as $C_2H_5NH_2$ becomes C_2H_5OH .

CHAPTER VII.

ABNORMAL VAPOUR DENSITIES AND DISSOCIATION.

WE have already seen the very great value of the determination of the density of substances in the state of vapour in assigning to them their molecular weights. There were for a long time, however, apparently very well marked exceptions to the rule, the best known of which are ammonium chloride and sulphuric acid.

The vapour density of ammonium chloride is 13·4 times that of hydrogen, and this indicates a molecular weight of 26·8. All other considerations, however, point to twice this, or 53·5, as being the most probable number; for example, it is formed by the direct union of one molecule of ammonia with one molecule of hydrochloric acid, the respective weights of which are 17 and 36·5. If we suppose the union gives rise to two molecules of ammonium chloride, each having a weight of 26·75, it is clear we must halve the atomic weights of nitrogen and chlorine. Another explanation, and, as we shall see, the correct one, is much simpler, and that is, that there is no vapour of ammonium chloride, but that when we heat solid ammonium chloride it separates into its two proximate constituents, and if these be allowed to cool they again reunite to form

solid ammonium chloride. In the same way we explain the very low density of the vapour from strong sulphuric acid. From its behaviour as an acid there is little doubt that it should be represented as H_2SO_4 , and if so, this necessitates a molecular weight of 98 and a vapour density of 49. Experiment, however, shows the true density of the vapour to be only half of this, viz., 24.5. This would involve, among other consequences, the atomic weight of sulphur being 16 instead of 32, and sulphuric acid being represented as a monobasic acid. The question is, then, Does the molecule H_2SO_4 exist as such in the state of vapour, or does it decompose into $\text{H}_2\text{O} + \text{SO}_3$? If the latter, this would explain the observed vapour density, as the 98 parts would be extended to twice the normal volume, and hence give half the normal density. We will consider the experimental proofs for these theoretical explanations above given.

When ammonia and hydrochloric acid gases are mixed at such a temperature that no solid is produced, we have no contraction in volume and no evolution of heat, and, in fact, no evidence of chemical change of any kind.

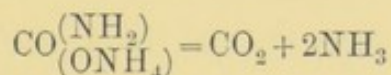
Ammonia gas is just about half as dense as hydrochloric acid, and therefore might be separated, partially at any rate, from the hydrochloric acid by utilising their different rates of diffusion, and we ought at the same time to find the excess of the hydrochloric acid remaining. Pebal showed this very clearly by a simple experiment, by heating some solid ammonium chloride in a glass tube with an asbestos partition. The gases evolved were carried away by a current of hydrogen (which has no effect on either gas). The result was

that the gases passing through the partition contained excess of ammonia, and when passed into red litmus solution turned it blue, and the gases which did not go through the partition reddened blue litmus, clearly proving, at any rate, that both ammonia and hydrochloric acid gases existed as such in the vapours from ammonium chloride.

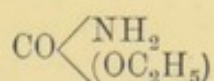
Further, Marignac has shown that the heat required to convert ammonium chloride into vapour is out of all proportion to that required to volatilise its constituents, but is practically equal to that evolved by their combination.

In a similar way sulphuric acid may be shown to dissociate, for if it be kept for some time in the condition of vapour in a flask with a small aperture, the water escapes by diffusion more rapidly, and the vapour inside the flask contains more molecules of sulphur trioxide than of water.

Ammonium carbamate, $\text{CO}(\text{NH}_2)(\text{ONH}_4)$, which is formed by the direct union of dry ammonia gas with carbon dioxide, breaks up into one volume of carbon dioxide and two volumes of ammonia, giving only one-third of the density required by the above formula—



The gases reunite on cooling. Ethyl carbamate, or urethane, is however quite normal, the vapour density corresponding to the formula



Another interesting example is calomel, or mercurous

chloride. It has long been known that although mercuric chloride could be purified by sublimation, calomel purified by washing with water was rendered more impure by being sublimed. Small quantities of both mercury and mercuric chloride were found to be present in the sublimed mass. Its vapour density is only half of that required by the formula Hg_2Cl_2 , which seems to be that most probable from general considerations, such as its analogy to cuprous chloride. It is true that HgCl could be adopted as its formula, and this would agree with its vapour density. But we know that without doubt its vapour consists of mercuric chloride and mercury, and that the small quantities of these which we always find in sublimed calomel are only those molecules which have lost one another, and got too cold to react on each other. If we adopted the formula HgCl it would mean that, if all the molecules behaved similarly, the mercury and chlorine atoms completely separated, and that then only one-half of the atoms of mercury combined with the molecules of chlorine which would be at the same time produced. If we adopt the formula Hg_2Cl_2 , each molecule breaks up into $\text{Hg} + \text{HgCl}_2$. By keeping a platinum tube cooled by water in the vapour from mercurous chloride, we can readily obtain mercury, or by exposing gold to the vapour it becomes coated with mercury, although it is quite unacted upon either by mercurous or mercuric chloride when the moist powders are rubbed on it.

Perhaps the most famous instance, however, is that of chloral hydrate, which was long regarded as a typical exception to Avogadro's law, or as a good instance of a "molecular compound." Its formula is $\text{CCl}_3\cdot\text{CHO}\cdot\text{H}_2\text{O}$,

or $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$. Chloral is a liquid boiling at $94\cdot5^\circ \text{C.}$, which readily combines with water to form the hydrate. The water is easily separated again by dehydrating agents, such as strong sulphuric acid. The density of the vapour from chloral hydrate is $41\cdot4$, which is only half what theory requires for the above formula. The boiling-points of chloral and of water being so near together prevents their separation by careful cooling. Troost devised a most ingenious test for the presence of water in the vapour, without any fear of decomposing even a very unstable compound, as a feeble dehydrating agent would do. He said, if it is completely decomposed into vapour of chloral and vapour of water, half of the pressure of the vapour will be due to the chloral and the other half to the steam. Many hydrated salts give off vapour of water in a dry atmosphere, but if the tension of aqueous vapour present be greater than that from the salt, no vapour will be given off. If, therefore, some hydrated salt (and the one selected was hydrated potassium oxalate, $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$) be placed in the vapour from chloral hydrate, at such a temperature that its tension is less than half of that yielded by the chloral hydrate, it ought not to give off any vapour of water; but if the vapour be truly a simple vapour, and containing no water as such, then the hydrated salt ought to decompose into anhydrous salt and water vapour. Now Wurtz showed that when the potassium oxalate was introduced no increase in the tension of the vapour was observed, conclusively proving that the tension of the vapour of water present in the chloral hydrate vapour was equal to or greater than that from the hydrated salt at the temperature.

In the cases given above we do not seem to have any of the compound in the state of vapour, or only a very small amount at most can exist, that is, we have no proof that the molecules NH_4Cl , H_2SO_4 , or $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ exist in the gaseous condition.

A very interesting case, in some respects resembling that of ammonium chloride, is that of amylene hydrobromate, $\text{C}_5\text{H}_{10}\text{HBr}$. When this is carefully volatilised at temperatures not more than about 40° above its boiling-point, we get the vapour density pointing to the formula $\text{C}_5\text{H}_{11}\text{Br}$; but if we make a series of determinations at various temperatures we find that the vapour density gradually diminishes till it again becomes stationary at exactly half what it was near the boiling-point. It is thus completely broken up into amylene, C_5H_{10} , and hydrobromic acid, HBr , which recombine on cooling, although never completely, the residue giving evidence as to what has happened. Here, then, we have, from 150° C. to 180° C. , a gas consisting of molecules of $\text{C}_5\text{H}_{11}\text{Br}$; and above 180° C. up to 360° C. , there are present, not only molecules of $\text{C}_5\text{H}_{11}\text{Br}$, but also of C_5H_{10} and HBr , and the two latter go on increasing as the temperature rises, while the first diminishes till it becomes extinct at 360° C.

Very many cases exist of this nature, and one which has been carefully studied is phosphorus pentachloride, the vapour density of which corresponds to neither that required for PCl_5 nor for $\text{PCl}_3 + \text{Cl}_2$ (unless at very high temperatures). The colour of the vapour is greenish-yellow, and this is rendered more apparent the higher the temperature. This points to a decomposition into $\text{PCl}_3 + \text{Cl}_2$, to some extent at least. Cahours said that

PCl_5 gave three volumes of vapour (taking the ordinary molecular volume = 2 volumes), or, in other words, its vapour density was only two-thirds of what its formula requires. This can be explained by supposing only half of it decomposes—



or 2 volumes becoming 3 volumes.

Let us try to picture what is taking place in the vapour under such circumstances. PCl_5 is constantly being decomposed into $\text{PCl}_3 + \text{Cl}_2$, which tend to reunite and reform PCl_5 , and as many decompositions as recombinations take place in a unit of time when the vapour density is constant. Suppose we mix the vapour with that of one of the constituents in a proportion similar to what we suppose to exist, we ought then to get a much larger number of recombinations from the much greater number of opportunities for recombination. Experiment fully bears out this explanation, for when we mix the vapour of phosphorus pentachloride with a sufficient quantity of that of the trichloride we have practically no decomposition at all.

Yet another case before we consider the vapour densities of some of the elements. Two bodies are known having the same percentage composition, and respectively represented by the formulæ NO_2 and N_2O_4 . The former is a dark-coloured gas, which condenses to a coloured liquid, the latter being in both conditions colourless. The dark colour of the vapour increases very rapidly with rise of temperature, in spite of the contrary effect produced by expansion. This, then, is a visible proof of the decomposition of N_2O_4 into 2NO_2 .

The following table shows the rate at which the change proceeds :—

Temperature.	Vapour Density.	Percentage decomposed into 2NO_2 .
26.7° C.	38.3	20.0
49.6	32.8	40.0
70.0	27.7	65.6
100.1	24.2	89.2
135.0	23.1	98.7
154.0	22.8	Total.

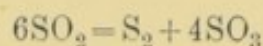
If we consider the vapour density of sulphur, it shows just the same thing; at about 500° C. it is about 96 times that of hydrogen at the same temperature, indicating a molecular weight of 192 and a formula S_8 ; but at about 1000° C. its density has fallen to 32, therefore its molecule has become S_2 , and it remains so apparently at the very highest temperatures yet tried. The halogens are by no means so stable, although at comparatively low temperatures the molecules consist of two atoms, yet on raising their temperature we get more and more molecules broken up into single atoms. This happens most readily with iodine, and the rate of the breaking up of its molecules is indicated in the following table :—

Temperature.	Vapour Density.	Percentage of Decomposition.
448° C.	126.2	...
764	119.6	...
940	110.5	14.5
1043	101.2	25.0
1275	84.0	50.5
1390	76.1	66.2
1468	73.1	73.1

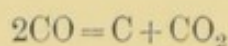
The density of chlorine diminishes, and according to V. Meyer, becomes stable at two-thirds of that required for Cl_2 . Oxygen and nitrogen are like sulphur, the atoms still being united in pairs at the highest temperatures; at least we have not been able to detect any breaking up by density determinations. Mercury likewise shows no decrease in its vapour density. This is, of course, what we should expect, as we assume its vapour to consist of isolated atoms at the lowest temperatures; and this condition apparently is general for the molecules of metals, Zn, Cd, K, Na, being the molecular formulæ for these substances.

The above cases of breaking up of molecules have been studied by the variations of their vapour densities from the normal ones. As the vapours cool they recombine, and the original solid or liquid is reformed. To decompositions of this class Deville applied the term *dissociation*, and the term *thermolysis* has also been applied to the same. One or two other methods of demonstrating the decomposition of bodies usually called stable, have been applied by Deville. Of these the neatest is the "hot and cold tube," in which we have an outer porcelain tube, which is placed in a furnace, it is closed at each end by a cork with two holes, one of which is in the centre of each stopper, and passing through these is a tube of some metal, such as silver; the other holes are fitted with tubes for the ingress and egress of the vapour under experiment. To use the apparatus, first a rapid stream of cold water is sent through the metal tube, then the temperature of the furnace is raised to a high temperature, and the vapour passed through. If we take as an example sulphur

dioxide, we find that the silver tube is blackened, and that the black substance is nothing but silver sulphide. We also find that the issuing gas contains sulphur trioxide, and that we have had the following decomposition:—



Similarly, carbon monoxide was decomposed into carbon, which was deposited on the cold tube, and carbon dioxide, which escaped with the unchanged monoxide—



Hydrochloric acid, even at 360°C ., has no action on silver amalgam, but on amalgamating the silver tube, and then transmitting a current of pure dry hydrochloric acid gas through the annular space between the tubes, the silver and mercury were converted into chlorides, and a small quantity of hydrogen was obtained on passing the issuing gases into water; here we have a proof that $2\text{HCl} = \text{H}_2 + \text{Cl}_2$ at high temperatures. In each of these cases we have conclusive evidence of decomposition having taken place, but have no measure of the extent. All we get is what has escaped recombination during the cooling. One thing clearly shown is, that at temperatures far below those which are produced by the combination of the elements, we have them existing in the free state in presence of each other. Nothing can make this clearer, however, than the experiments of Grove and others on water. If platinum be heated till it melts, by means of the oxyhydrogen blow-pipe, that is, at a temperature produced by the union of hydrogen with oxygen, and then poured into cold water which has been recently boiled, along with the steam

we have bubbles of permanent gas ascending from the platinum to the surface of the water. On examining this gas by passing an electric spark through it, we have an explosion followed by contraction, almost the whole of the gas disappearing, steam having been produced and then condensed. The permanent gases were evidently a mixture of hydrogen and oxygen. The water had been decomposed by the passage through it of the intensely heated platinum which, however, could not be at a temperature higher than that produced by the combination of the two elements, but was even when at its hottest sensibly below it. Water, then, can be decomposed into its elements at temperatures far below that produced by the union of these elements when it is the product. A modification of this experiment, which is not only far more easily performed but exhibits the dissociation at much lower temperatures, is to blow the steam from water which has been boiling for half an hour, over a coil of platinum wire kept incandescent by the passage through it of a galvanic current, into cold boiled water. The instant that the wire is heated, the sharp crackling sound, produced by the pure steam condensing in the cold water, is changed to the muffled sound from the condensation of the steam mixed with permanent gas. In this way it is easy to collect many cubic centimetres of explosive gas in a short time.

If, then, steam be so readily broken up by a temperature at which platinum is not melted, what must be the constitution of a flame produced by the union of hydrogen and oxygen? 1 gram of hydrogen unites with 8 grams of oxygen to form 9 grams of water, and with the evolution of 34,500 heat units. If we suppose all this

to be retained in the steam produced, and that the combination is instantaneous, we find that we ought to have a temperature of about 6800°C . This is clear from the following:—The 34,500 units are due to the heat evolved in the formation of steam from its elements + the latent heat of the 9 grams of steam + the heat given out by the water at 100°C ., falling to 0°C .

Since the specific heat of steam is sensibly the same as that of the mixture of hydrogen and oxygen, $= .475$, we get

$$\begin{array}{rcl}
 34500 = \left\{ \begin{array}{l} = 9 \times 100 \\ + 9 \times 537 \\ + 9(.475)(T. - 100) \end{array} \right. & \begin{array}{l} = \\ = \\ = \end{array} & \begin{array}{l} 900 \\ 4833 \\ 4.275T. - 427 \end{array} \\
 & & \hline
 \therefore 34500 & = & 4.275T. + 5306 \\
 29194000 & = & 4275T. \\
 6829^{\circ} & = & T.
 \end{array}$$

Many attempts have been made to determine the highest temperature of the oxyhydrogen flame, but no one has obtained anything like so high a result as that calculated above. Apparently it does not exceed 2300°C .

What is then the cause of this great discrepancy?

It has been clearly proved that the heat generated by the union of two bodies to form a compound is exactly equal to that required to decompose that compound into those constituents. Then the heat given out by 1 gram of hydrogen, combining with 8 grams of oxygen, is exactly that required to decompose the 9 grams of steam back into its elements. Are we then to suppose that no chemical change will take place? The real change is a gradual one, or we may imagine

instantaneous combination of the whole, and then a decomposition to a certain extent, accompanied with fall of temperature, so that, at the temperature now attained, we may have a stable mixture of hydrogen, oxygen, and steam. As heat is allowed to escape or is abstracted, we have a lower temperature produced, and then a larger proportion of the elementary gases unite till the union is complete. Deville showed this actually to be the case by mixing carbon monoxide and oxygen in the proportions in which they combine; and then igniting the mixture at a jet, by a very simple method he was able to draw samples of the gases from any part of the flame, and then determine the composition of the mixture. He found that at the hottest part of the flame more of the separate gases existed in proportion to the compound formed; but as he took samples higher and higher in the flame he got relatively lower and lower temperatures, and at the same time more and more of the compound, till, at the tip of the flame, carbon dioxide was found free from the monoxide. A very instructive instance is that of hydriodic acid gas, which is both readily formed and readily decomposed at comparatively low temperatures. If we mix exactly equal volumes of hydrogen and iodine vapour, and pass them together through a long heated tube containing spongy platinum, and then analyse the gaseous mixture which comes out of the tube, we find it to be identical in composition with that obtained by passing dry hydriodic acid gas through the tube at the same temperature, but that for every different temperature there is a new ratio amongst the components. The stability of the compound varies with the temperature, and the gaseous mixture consists of

compound molecules breaking up into their elements, and the converse, the elements reuniting to form the compound. When an equal number of compound molecules are decomposed and reformed in unit of time, we have got the stable composition of the gaseous mixture. By varying the temperature, we either accelerate or retard this rate, and so the composition of the mixed gases varies.

It is much easier to follow the effects of temperature on the dissociation of a substance which, by its breaking up, gives rise to only one volatile component, and one of the simplest is the dissociation of calcium carbonate into calcium oxide (lime) and carbon dioxide. Here we may determine the pressure exerted by the gas evolved, and we find that for every definite temperature there is a perfectly definite pressure of gas, corresponding in exactly the same way that we have the vapour tension from a fluid depending on its temperature. This is often called the "tension of dissociation." To study the dissociation of calcium carbonate we may use a hard glass tube, or better one of porcelain, closed at one end, and connected with a manometer and a mercurial air-pump. In the tube is placed carefully dried calcium carbonate, and the apparatus completely exhausted. Heat the calcium carbonate first to the boiling-point of mercury. This causes no visible movement of the mercury in the manometer, nor does the temperature of boiling sulphur produce any measurable tension, although it is sufficient to dim the surface of bright crystals of Iceland spar. At the boiling-point of cadmium the tension is 85 mm., and the boiling-point of zinc gives 520 mm. If we were now to remove the atmosphere of carbon

dioxide from the tube, and again allow the apparatus to remain untouched, the gas would, after a time, attain the same tension of 520 mm. ; and this may be repeated as long as we have carbon dioxide present sufficient to fill the tube to this tension. The amount of free lime present has no effect, nor has the excess of calcium carbonate. If, then, we have removed all the carbon dioxide, and have nothing but pure lime in our tube, and pass into the apparatus pure carbon dioxide till we have it filled at the atmospheric pressure, the lime and the gas will combine till we have the same tension indicated as before ; and this addition of carbon dioxide can be repeated, just as its removal, till, in this case, there is no more free lime to combine with the last charge of the gas.

We have here clearly the two processes going on at the same time—calcium carbonate breaking up into its constituents, and these two constituents reuniting to form the compound again. When these two processes are going on at the same rate we have the tension of the gas constant ; but if we allow the temperature to rise to a definite point, we have more decomposition than recombination, and the tension increases until it again becomes stationary and records its value corresponding to the new temperature. If the temperature be lowered and kept stationary for some time, we have the combination more rapid than the breaking up, and a correspondingly smaller tension is now recorded.

This is exactly parallel to what happens when a liquid is heated and cooled in presence of its vapour. Now, it is well known that not only can a liquid be much more rapidly evaporated in a current of an inert

gas but also at a much lower temperature. This is also what happens in such a case as we have been considering. Gay Lussac remarked that calcium carbonate decomposed much more easily in an open vessel than in one closed so that the carbon dioxide could not be displaced by the external air. He showed also that when he decomposed it in a porcelain tube, and allowed the temperature to fall, so that carbon dioxide was no longer expelled at the atmospheric pressure, on subjecting it to the action of a current of steam, gas came off with great ease. What happened was obviously that the decomposition and recombination, which were equal in amount until the passing of the steam, were made very unequal by the removal of the gas from the field of action preventing recombination, while the decomposition went on as before. Everyone knows that, to prepare lime from limestone or marble, it is done in a current of air or other inert gases; on the small scale in the laboratory, by placing the marble in a crucible with the bottom perforated so as to allow a current of air to pass through it, the use of the crucible being merely to prevent contamination from contact with the ashes of the fuel, &c.; on the large scale, the limestone and fuel are mixed or put in alternate layers in a kiln, and the stone dissociates in the current of nitrogen and oxides of carbon, and the quicklime is removed at the bottom of the kiln.

The effect of a current of air in decomposing the carbonate is well seen by taking two tubes and placing in each some clear crystals of Iceland spar, then placing the tubes side by side in a furnace and raising the temperature, so that the tension of the carbon dioxide is

well under that of the atmosphere. Pass through the tubes a current of air and of carbon dioxide respectively, when we will find that after some time the crystals in the air current are quite opaque and those in the other retain their brilliancy.

Another very interesting substance is barium dioxide, the dissociation of which is employed on the large scale for the manufacture of pure oxygen from the atmosphere. The average atmospheric pressure being 760 mm., gives for the two gases in pure air the following tensions:—For nitrogen, 603 mm., and for oxygen, 157 mm. If we heat barium *monoxide* in dry air to such a temperature that the tension of the oxygen from the *dioxide* is less than 157 mm., we ought to have the dioxide formed, and this ought to go on if fresh air be supplied until the whole of the monoxide is converted into dioxide. To dissociate this, all that is required is to raise the temperature sufficiently to evolve the oxygen at the atmospheric pressure, that is, until the tension of dissociation exceeds 760 mm.

The experiments with calcium carbonate suggest another mode of obtaining the oxygen without varying the temperature, and that is to remove the atmosphere of oxygen by means of an air-pump. The dioxide will continue to give off oxygen as long as its tension is kept below the maximum corresponding to its temperature. This is now carried out on a large scale, and has superseded the older form of the process when the oxide was heated to a low red heat in a current of air, and then the temperature raised. The alternate cooling and heating of the vessels rapidly destroyed them, and the subjecting of the oxide to a very high temperature

tended partially to vitrify it and render it incapable of combining with oxygen at the lower temperature.

A very important problem was to determine how limestone became marble. The crystalline appearance of marble indicates that it has undergone fusion, but we have seen above that on moderate heating it becomes lime without exhibiting any traces of fusion. Sir James Hall showed, however, that if the carbon dioxide be prevented from escaping, the limestone may be fused, but only under great pressure; and this may be seen in nature, in Teesdale, for example, where the whinstone has apparently been run on the limestone at great depths, and the carbon dioxide having been unable to escape, the limestone has not been perceptibly decomposed, but became metamorphosed into marble by the high temperature due to its contact with the melted whinstone.

If compounds have a definite tension of dissociation, we may use this property as a test for the existence of compounds and distinguish them from mixtures. Before examining doubtful cases, the study of some compounds which ammonia forms with metallic chlorides will show clearly how we may apply our test.

Two compounds of silver chloride are known, one with twice as much ammonia as the other, and having the formulæ $\text{AgCl} \cdot 3\text{NH}_3$ and $2\text{AgCl} \cdot 3\text{NH}_3$. The tensions of the ammonia from these are:—

$\text{AgCl} \cdot 3\text{NH}_3$		$2\text{AgCl} \cdot 3\text{NH}_3$	
T.	Millim.	T.	Millim.
0·0	293	34·2	1713
10·6	505	48·5	2414
17·5	655	51·5	4132
24·0	937	54·0	4641
28·0	1355	57·0	4880

2AgCl.3NH ₃		2AgCl.3NH ₃	
T.	Millim.	T.	Millim.
20·0	93	77·5	1198
31·0	125	83·5	1593
47·0	268	86·1	1813
58·5	528	88·5	2013
69·0	786	103·0	4800
71·5	946		

If we begin with the first compound and remove ammonia by stages from it, keeping it at one definite temperature, we will find that after each removal of ammonia it will recover its full tension till a point is reached when its tension will no longer be nearly as much as before; but that, if we still continue to remove ammonia, this new tension will be constant for a considerable range as for the former compound, but we have no intermediate tensions. It is either that for the one or for the other compound.

Let us see how this may be applied to the study of the condition of hydrogen in palladium. The temperature at which the tensions were measured was about 100° C. :—

Fused Palladium.		Spongy Palladium.	
Vol. of Hydrogen.	Tension.	Vol. of Hydrogen.	Tension.
809	1482	775	715
743	909	743	493
700	598	718	361
672	454	684	247
642	353	608	227
509	238	590	225
456	225	300	224
420	230		

Here evidently, to commence with, we have hydrogen in excess of what is required for the compound, and as we remove it the tension falls till it becomes constant at about 600 volumes of hydrogen in 1 of palladium, and remains so till most of the hydrogen is removed.

This agrees with the formula Pd_2H (not PdH_2 , as usually given), for

600 c.c. of hydrogen weigh about 00·5376 grams.

1 c.c. of palladium „ 11·4 „

·05376 :: 11·4 :: 1 : 212 :: H : Pd_2

It is well known that carbon absorbs very large quantities of various gases, and retains them to a considerable extent even *in vacuo*. Does carbon combine with ammonia gas, for example, in the same way that palladium combines with hydrogen? The following series of tensions show no evidence of any definite tension corresponding to any compound, but, on the contrary, the temperature remaining the same, the tension varies according to the volume of absorbed gas more or less directly. The carbon was heated for some time *in vacuo*, and the gases it contained extracted by means of an air-pump, and after cooling it was saturated with pure dry ammonia, which it absorbed with evolution of considerable heat. The charcoal was now enclosed in a tube connected with a manometer and air-pump, and the gas removed in small quantities.

An experiment at 19° C. gave these tensions (in millimetres)—

226	144	104
205	138	98
188	131	94
174	123	91
164	116	88
154	110	

One at 100° C. gave—

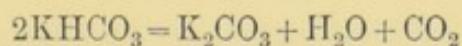
358	118
272	104
214	89
191	71
141	61

Applying the same method to a solution of ammonia gas in water in order to obtain, if possible, evidence of the compound NH_4OH , corresponding to the well-known $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$, and analogous to KOH , Isambert got the following results:—

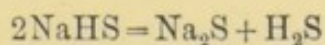
Between $21^{\circ}5$ and $22^{\circ}5$, Millim.	At 48° Millim.	At 100° Millim.
636	514	1764
510	502	1478
490	485	1248
474	472	1009
460	465	
423	453	
398		
373		

We see clearly that this is of the same nature as the carbon and ammonia—no fixed tension for a fixed temperature—and conclude that our substance has not that fixity of composition which is an essential of a true compound.

If we dissolve many salts in water, we can easily obtain evidence of their dissociation if one of the products should be a gas. For example, if well-crystallised potassium bicarbonate be dissolved in water, and a current of an inert gas, such as nitrogen, be passed through the solution, we get it to remove carbon dioxide, and leave a solution of the carbonate—

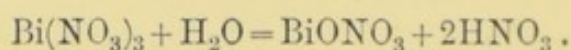


In the same way sodium hydrogen sulphide breaks up, and hydrosulphuric acid is readily removed by a current of hydrogen, which is the best gas to use for this—



In a similar way we have many salts decomposed by water and precipitates produced. Perhaps the best known are the normal salts of bismuth, which readily break up into a basic salt and free acid. The larger the quantity of water the more salt must be decomposed to give the necessary number of molecules of acid per molecule of salt to keep it stable, or at least in solution. We have here, then, a corresponding phenomenon to that presented by phosphorus pentachloride in the state of vapour.

If water be poured on the crystals of the normal bismuth nitrate, $\text{Bi}(\text{NO}_3)_3 + 5\text{H}_2\text{O}$, we get a crystalline white powder formed and nitric acid set free,

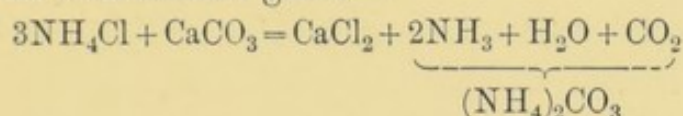


When we have about 82 grams of free nitric acid per litre there is no further decomposition, and the normal nitrate dissolves, and according as we add nitric acid or water we get either basic nitrate reconverted or normal nitrate decomposed, so as to maintain the liquid at the proper strength in nitric acid. The composition of the basic nitrate is $\text{BiONO}_3 + \text{H}_2\text{O}$ or $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 + 2\text{H}_2\text{O}$, and if this be washed with much cold water it further breaks up into $2\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5$ and free nitric acid. Warm water does the same, and seems to decompose the BiONO_3 when the liquid at 100°C . contains about 4 grams per litre of nitric acid, and if the crystalline subnitrate be boiled with water containing that amount of nitric acid it remains bright and sparkling, but if there be less than 4 grams per litre the liquid immediately becomes turbid, and passes so through a filter, while the crystals lose their bright-

ness ; but, as in the other case, if nitric acid be added to this opalescent liquid, we again get the crystalline powder reformed.

In the same way, but more completely, is the chloride decomposed by water. Antimony trichloride, mercuric sulphate, and many other salts, behave similarly.

That ammonium salts dissociate in solution is easily shown by boiling a neutral solution of the chloride or sulphate. The ammonia is removed by the current of steam, and the much less volatile acid remains behind, and is easily detected. If ammonium chloride be boiled with calcium carbonate, we get calcium chloride in solution and ammonium carbonate volatilised in the form of its constituent gases—



for as soon as any ammonium chloride is dissociated and the ammonia removed, the hydrochloric acid attacks the calcium carbonate and becomes neutralised, a further quantity of ammonia is then expelled, and more of the carbonate dissolved till the reaction is complete. If this reaction be carried out in a flask with a condenser, and the distillate be added to the residue in the flask when cold, the whole system will return to its original condition, viz., solution of ammonium chloride and a precipitate of calcium carbonate.

The bicarbonates of the alkali metals are decomposed in a similar manner ; on boiling their solutions we have the carbon dioxide coming off with the steam, and the normal carbonate remains in solution. Use is made of this decomposition in the titration of the alkalis when litmus is used as the indicator.

CHAPTER VIII.

PHYSICAL PROPERTIES OF COMPOUNDS.

IN Chapter I. we have seen the relation existing between the density of a gas or vapour and the relative weight of its molecules. We use the term specific gravity to express the density of substances relatively to a standard substance—water for solids and liquids, and air and hydrogen for gases and vapours. Since volume is mass divided by density, we use also the term specific volume to express the volume of equal masses of the substances, and if we multiply this by the molecular weights we get what is known as the molecular volume of the substance; and for solids and liquids this is the number of cubic centimetres occupied by the molecular weight in grams of the substance. The molecular volume of all gases is the same, and is 2 if we take hydrogen as our standard and 28·94 if air, as

	Oxygen,	molecular weight	=	$32 \div 16$	(H = 1)	=	2
or							
	"	"	"	$32 \div 1\cdot1056$	(air = 1)	=	28·94
or							
	Chlorine,	"	"	$71 \div 35\cdot5$		=	2
	"	"	"	$71 \div 2\cdot46$		=	28·94

With regard to liquids and solids, both elementary and compound, several very important and interesting

relationships have been shown to exist between the specific and molecular volumes and their chemical properties and constitution. As the rate at which liquids and solids expand depends on the individual substance, and is unlike the rate of gaseous expansion, we must carefully specify the temperatures at which the specific volumes are taken, and also endeavour to select such temperatures as may enable us to compare the substances when in similar thermal conditions. With regard to liquids, which we shall consider first, it was soon found that one temperature, say 0°C. , was not a suitable one, and the temperatures usually selected are those at which the liquids have the same vapour tension, and hence we take as the simplest that of their boiling-points under 760 mm. pressure. Kopp, in 1842, in trying to trace connections between the constitution and the physical properties of organic bodies chiefly, found that not only did the boiling-points rise regularly with a definite increase in the composition of the molecule, but that the molecular volume was augmented in a similar manner. To take one or two examples—

	Mol. Wt.	Diff.	Mol. Vol.	Diff.	Boiling-Point.	Diff.
Formic acid, $\text{H}-\text{CO.OH}$,	46	$\text{CH}_2=14$	42	22	99°	19°
Acetic acid, $\text{CH}_3-\text{CO.OH}$,	60		64		118°	
Propionic acid, $\text{C}_2\text{H}_5-\text{CO.OH}$,	74	$\text{CH}_2=14$	86	22	$140^{\circ}\cdot7$	$22^{\circ}\cdot7$
Butyric acid, $\text{C}_3\text{H}_7-\text{CO.OH}$,	88		108		163°	
Valerianic acid, $\text{C}_4\text{H}_9-\text{CO.OH}$,	102	$\text{CH}_2=14$	130	22	$184^{\circ}\cdot5$	$21^{\circ}\cdot5$

From this we see that an increase in the molecule of an

atom of carbon and two atoms of hydrogen produces an increase of 22 in the molecular volume, or that the molecular volume of $(\text{CH}_2) = 22$.

The molecular volumes of metameric bodies are the same, as *but see exceptions on the following pages—*

		Molecular volume (experimental).
Methyl valerate, .	} $\text{C}_6\text{H}_{12}\text{O}_2$. .	148·7–149·6
Ethyl butyrate, .		149·1–149·4
Butyl acetate, .		149·3
Amyl formate, .		149·4–150·6

The substitution of an atom of carbon for two atoms of hydrogen does not change the molecular volume of compounds of the same chemical type, as

		Observed.
Valeraldehyde, $\text{C}_5\text{H}_{10}\text{O}$, . .	.	117·3
Benzoic aldehyde, $\text{C}_7\text{H}_6\text{O}$, . .	.	118·4
and		
Ethyl valerate, $\text{C}_7\text{H}_{14}\text{O}_2$, . .	.	173·5–173·6
Ethyl benzoate, $\text{C}_9\text{H}_{10}\text{O}_2$, . .	.	172·4–174·8

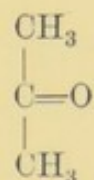
Hence, as a difference of (CH_2) in the composition produces a difference of 22 in the molecular volume—and we have just seen that the replacement of one atom of carbon by two atoms of hydrogen causes no change—we say that the change produced by (C) is equal to that produced by (H_2) , and that each is equal to $\frac{22}{2} = 11$; and hence $(\text{H}) = 5·5$ and $(\text{C}) = 11$.

In liquid compounds of the same chemical type, the replacement of two atoms of hydrogen by an atom of oxygen produces very little alteration in the molecular volume. This is readily seen by comparing alcohols with the acids produced from them by oxidation, as

	Molecular volume (experimental).
Ethyl alcohol, C_2H_6O , . . .	61·8– 62·5
Acetic acid, $C_2H_4O_2$, . . .	63·5– 63·8
Ethyl ether, $C_4H_{10}O$, . . .	105·6–106·4
Ethyl acetate, $C_4H_8O_2$, . . .	107·4–107·8
Acetic anhydride, $C_4H_6O_3$, . . .	109·9–110·1

In every case, however, we have a slight increase resulting from the substitution, and may conclude that the atomic volume of oxygen exceeds twice that of hydrogen by a definite, although small, quantity. But if we take two metameric bodies of different constitution, especially as regards the oxygen, such as acetone and allyl alcohol, one a ketone, the other an alcohol, both having the same empirical formula, C_3H_6O , we find the former has a much higher molecular volume, 78, whilst the other is 74. The molecular volume of water is 18·8, and if we subtract 11 from it for the two hydrogen atoms, we get only 7·8 for an atom of oxygen united to *two different atoms*; yet when we oxidised alcohol, the value seemed to *exceed* 11. From the consideration of many substances, Kopp fixed the value for oxygen, when united to *one carbon atom alone*, as 12·2.

In acetone we have two methyl groups united to (C=O) thus—

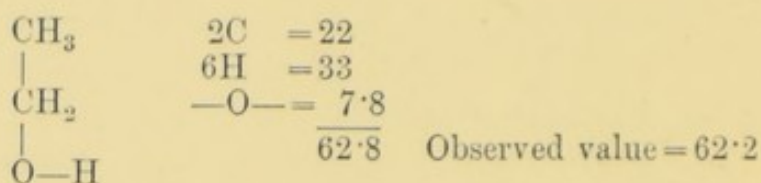


Its atomic volume ought to be

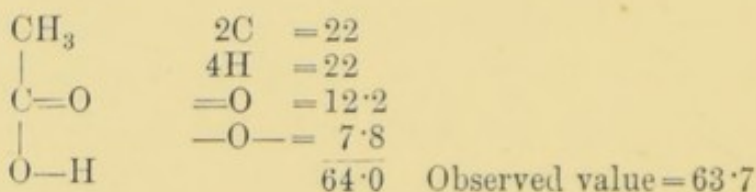
$$\begin{array}{rcl} 3C & = & 3 \times 11 = 33 \\ 6H & = & 6 \times 5\cdot5 = 33 \\ =O & = & 1 \times 12\cdot2 = 12\cdot2 \\ & & \hline & & 78\cdot2 \end{array}$$

The observed value is 77·6.

Ethyl alcohol—



Acetic acid—



In the same way it has been found that sulphur has two values, 28·6 when it is united to only one atom, and 23·0 when united to two atoms.

Chlorine, bromine, and iodine have each only one value, and these values are respectively

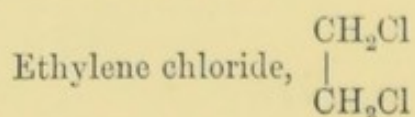
$$\text{Cl} = 22\cdot8$$

$$\text{Br} = 27\cdot8$$

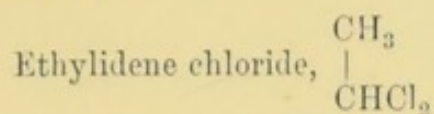
$$\text{I} = 37\cdot5$$

For nitrogen three values are often given, viz., 2·3 in amines, 17 in cyanogen compounds, and 17·4 in nitro-compounds, but these are somewhat unsatisfactory.

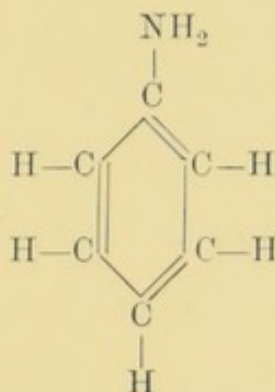
It was stated above that metameric bodies had the same molecular volume. This is not strictly true in all cases, even when they are of similar constitution. We have seen how the molecular volumes of acetone and allyl alcohol differ, since the atomic volume of oxygen is in the former 12·2, and only 7·8 in the latter. If, however, we compare the two dichlorethanes we have the molecular volume 85·34 for



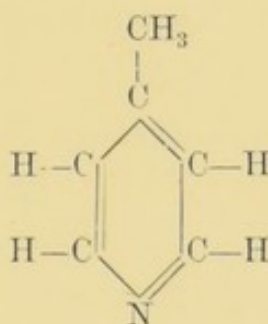
but 88.96 for that of



Again, for aniline, $\text{C}_6\text{H}_5\cdot\text{NH}_2$, the molecular volume is 106.37.



but for picoline, $\text{C}_5\text{H}_4\text{N}\cdot\text{CH}_3$, it is 111.50.



The difference in many instances between the observed and the calculated values is too great to be put down to experimental errors, and is very often associated with unsaturated bodies, and especially the aromatic compounds, as

	Molecular volume.		Difference.
	Calculated.	Observed.	
Benzene, C_6H_6 ,	99	95.8	3.2
Cymene, $\text{C}_{10}\text{H}_{14}$,	187	183.5	3.5
Benzoic aldehyde, $\text{C}_6\text{H}_5\cdot\text{CHO}$,	122.2	118.4	3.8
Benzyl alcohol, $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{OH}$,	128.8	123.7	5.1

It has been suggested, that instead of the elements themselves having atomic volumes, we might have several groups of atoms, each having the same specific volume; and, in many cases, the values got in this way agree with the observed values almost as well as those calculated by the other hypothesis. If we take O_2 (in carboxyl), CH_2 , H_2O , and CO as all having the same volume, 20·8, we get for

			Calculated.	Experiment.
Formic acid, .	CH_2O_2	$2 \times 20\cdot8$	= 41·6	41·8
Acetic acid, .	$2(CH_2)O_2$	$3 \times 20\cdot8$	= 62·4	63·4
Ethyl Alcohol, .	$2(CH_2)H_2O$	$3 \times 20\cdot8$	= 62·4	62·2

Schröder gives the series of alcohols and acids—

			Molecular volume.	
Methyl alcohol, .	$CH_4O = CH_2 + H_2O$	42·3	= $2 \times 21\cdot2$	
Ethyl alcohol, .	$C_2H_6O = 2(CH_2) + H_2O$	62·2	= $3 \times 20\cdot7$	
Propyl alcohol, .	$C_3H_8O = 3(CH_2) + H_2O$	81·5	= $4 \times 20\cdot4$	
Butyl alcohol, .	$C_4H_{10}O = 4(CH_2) + H_2O$	102·3	= $5 \times 20\cdot5$	
Amyl alcohol, .	$C_5H_{12}O = 5(CH_2) + H_2O$	122·8	= $6 \times 20\cdot5$	
Formic acid, .	$CH_2O_2 = CH_2 + O_2$	41·8	= $2 \times 20\cdot9$	
Acetic acid, .	$C_2H_4O_2 = 2CH_2 + O_2$	63·4	= $3 \times 21\cdot1$	
Propionic acid, .	$C_3H_6O_2 = 3CH_2 + O_2$	85·9	= $4 \times 21\cdot5$	
Butyric acid, .	$C_4H_8O_2 = 4CH_2 + O_2$	108·0	= $5 \times 21\cdot6$	
Valerianic acid, .	$C_5H_{10}O_2 = 5CH_2 + O_2$	130·4	= $6 \times 21\cdot7$	

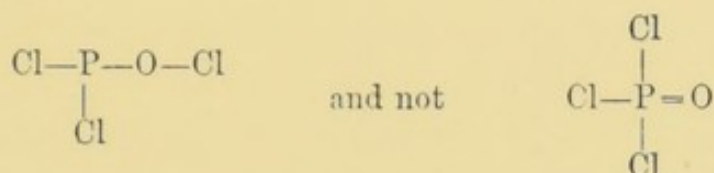
We need hardly pursue this subject any further at present, as it is very evident that we must have many more observations of specific volumes carried out on series of substances produced by repeated substitution as well as by continuous abstraction of elements.

The problems which have been attacked by the aid of our knowledge of specific volumes are such as the constitution of bodies like $POCl_3$, whether it ought to be represented as $O=P\equiv Cl_3$ or $Cl_2=P-O-Cl$, that is, whether phosphorus is a pentad or triad in phosphorus

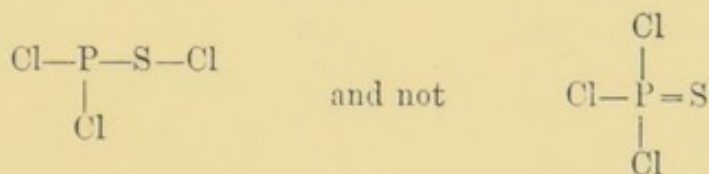
oxychloride, and it is a case which well illustrates the difficulty of obtaining definite information. The atomic volume of phosphorus, as determined from the element, is 20·9 (Ramsay and Masson), 20·2 (Pisati and De Franchis).

The molecular volume of phosphorus oxychloride, POCl_3 , is 101·3, that of the trichloride is 93·4; 101·3-93·4 gives 7·9 for the oxygen.

Hence we may conclude that the oxygen is united to different atoms in this case, one of phosphorus and one of chlorine, and that the constitution may be expressed by



for this would have required $\text{O} = 12\cdot2$. In the same way we have the molecular volume of thiophosphoryl chloride, $\text{PSCl}_3 = 116\cdot1$, and of the trichloride, as before, 93·4; $116\cdot1 - 93\cdot4 = 22\cdot7$ for the atomic volume of sulphur in this compound, and its constitution



which would require $\text{S} = 28\cdot6$.

Ramsay, however, points out that if in the molecular volume of the oxychloride, we consider the oxygen as doubly united to the phosphorus, we obtain for phosphorus the same value as he had found directly from the element—

184 ATOMIC VOLUME OF PHOSPHORUS.

Molecular volume of POCl_3 ,	101.4
$\text{O} = 12.2 + (3\text{Cl.} = 3 \times 22.7 = 68.1)$	80.3
Atomic volume of phosphorus,	21.1

Similarly from the thiophosphoryl chloride we get the atomic volume of phosphorus, 19.9

And from the chloro-bromide, POCl_2Br , 21.7

Giving as a mean, 20.9

In pentad compounds, and in the free state, we have 20.9

In the triad compounds we have PCl_3 , 93.4

„ „ 3Cl , 68.1

Atomic volume of phosphorus, = 25.3

As phosphorus is a member of the same chemical family as nitrogen, it is almost certain to have, like it, more than one value for its atomic volume.

The atomic volume of sulphur, determined by Ramsay from the element, gave 21.6 as a mean, which is almost that of sulphur united to two different atoms.

Our knowledge of the connection between the volume of solids and their chemical composition or constitution is at present very limited. We have, however, already seen (Table and curve, p. 70) how the atomic volume varies with atomic weight. With regard to solid compounds certain relations have been observed, the most general being that the molecular volumes of isomorphous compounds are equal—

		Molecular weight.	Specific gravity.	
Strontianite,	SrCO_3	147.5	3.6	= 41
Cerussite,	PbCO_3	267	6.5	= 41

		Molecular weight.	Specific gravity.	Molecular volume.
Vitriols—				
Magnesium sulphate,	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	246	1.68	146
Zinc sulphate, .	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	287	2.015	142
Nickel sulphate, .	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	281	1.98	142
Cobalt sulphate, .	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	281	1.924	146
Ferrous sulphate, .	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	1.884	147

Alums—

Potassium alum,	$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	474	1.72	275
Sodium alum, .	$\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	458	1.6	286
Ammonium alum,	$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	453	1.624	279
Chromium alum,	$\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	499	1.84	271

Chlorides—

Potassium chloride, .	KCl	74.5	1.98	37.4
Sodium chloride, .	NaCl	58.5	2.15	27.2
Strontium chloride, .	SrCl_2	158.5	3.05	50.3
Barium chloride, .	BaCl_2	208	3.85	54
Silver chloride, .	AgCl	143.5	5.55	25.8
Mercuric chloride, .	HgCl_2	271	5.42	50
Lead chloride, .	PbCl_2	278	5.8	48
Cuprous chloride, .	Cu_2Cl_2	198	3.53	56.1
Cupric chloride, .	CuCl_2	134.5	3.05	44.1

Bromides—

Potassium bromide, .	KBr	119	2.69	44.2
Sodium bromide, .	NaBr	103	3.014	34.1
Strontium bromide, .	SrBr_2	247.5	3.962	62
Barium bromide, .	BaBr_2	297	4.23	70
Silver bromide, .	AgBr	188	6.35	29.6

The above examples give an idea of the approximation to the law above stated, exhibited by different classes of bodies.

Playfair and Joule pointed out that the volumes of many hydrated salts are exactly the same as that of the water they contain, if it were in the solid form (as ice). The particles of the salt then seem to be intercalated

amongst the pores of the ice, so as to increase the density, but without increasing the volume.

		Mol. Wt.	Volume.		Specific Gravity.	
			Expt.	Theor.	Expt.	Theor.
Sodium car- bonate, }	$\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}, .$	286	197.2	196	1.454	1.463
Disodium hydrogen orthophos- phate, }	$\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O},$	358	235.5	235.2	1.525	1.527
Trisodium orthophos- phate, }	$\text{Na}_3\text{PO}_4 + 12\text{H}_2\text{O}, .$	380	235.2	235.2	1.622	1.622
Cane-sugar,	$\text{C}_{12}\text{H}_{22}\text{O}_{11}, . . .$	342	214.3	215.6	1.596	1.591
Disodium hydrogen arsenate, }	$\text{Na}_2\text{HAsO}_4 + 12\text{H}_2\text{O},$	402	232.0	235.2	1.736	1.713
Trisodium arsenate, }	$\text{Na}_3\text{AsO}_4 + 12\text{H}_2\text{O}, .$	424	235.6	235.2	1.804	1.808

We may notice that the water existing in the salt, and taking the place of soda in the acid salts, does not behave like the water of crystallisation, although the hydrogen and oxygen in the cane-sugar (and milk-sugar also), which are in the proportion required to form water, behave exactly like the water of crystallisation in the other salts.

The connection between the volume of many crystallised salts, and that of the water and the anhydrous salt they contain, is much more complicated, *e.g.*, the alums.

Many chemical compounds in their various physical states exercise a definite action on light, and one of the most interesting, as well as the simplest, is the velocity of light in that medium relatively to that in another

which may be a vacuum, but more generally air. This constant is known as the index of refraction, and is usually measured by the deflection of a ray of light by means of a prism of known angle. For liquids a triangular bottle made of glass plates with parallel sides, is generally used. As the rays are very differently bent according to their colour or wave-length, it is always necessary to state for what wave-length the index of refraction has been determined, those in common use being the Fraunhofer line C (red hydrogen line), the red lithium line, or the D line (yellow sodium line). A ray of such light entering, say, water from air, and making an angle i with the perpendicular to the common surface of the two media, makes now an angle r in the new medium with the perpendicular. Although the amount of bending depends on the original inclination of the ray, the ratio of the sines of the angles is a constant, $\frac{\sin i}{\sin r}$ = index of refraction which we shall call n . But the effect of temperature on all substances is to change their densities and also their refractive indices, and various formulæ of an empirical nature have been given so as to obtain an expression independent of the temperature, the simplest being $\frac{n-1}{d}$, d being the density. This is called the specific refraction, and if we multiply this by the molecular weight we get what is termed the molecular refraction of the substance.

As we saw with regard to the molecular volumes of liquids, it will be necessary to make very many more determinations with the highest attainable accuracy before we can enunciate the laws expressing the relationship

between chemical composition and the velocity of light in chemical compounds. The study of organic bodies in this respect is both easier and more likely to give definite information than the study of inorganic bodies, the constitutions of which have not been worked out in the same detail as those of the carbon compounds. The compounds of carbon being in so many cases liquid, further much facilitates the accurate determination of the data required. The study of a large number of liquid compounds, chiefly belonging to the fatty series, has led to the following general results:—

1. Isomeric bodies have the same molecular refraction.
2. The addition of two atoms of hydrogen (H_2) to the molecule increases the molecular refraction by 2·6.
3. The difference in the molecular refraction between one member of a homologous series and the next member is 7·6, which corresponds to a difference in chemical composition of (CH_2) .
4. The acetic acid series has the general formula $C_nH_{2n}O_2$, and the molecular refraction of its members is $7·6n + 6$.

It is evident that we possess sufficient data to determine the atomic refraction of carbon, hydrogen, and oxygen, for we have—

$$\begin{aligned} H_2 &= 2·6 \\ CH_2 &= 7·6 \\ O_2 &= 6·0 \end{aligned}$$

Whence we get that of—

$$\begin{aligned} H &= 1·3 \\ C &= 5·0 \\ O &= 3·0 \end{aligned}$$

At 20° C. the density of ethyl alcohol is ·800, and its index of refraction is 1·3624—

$$\frac{n-1}{d} = \frac{1\cdot3624-1}{\cdot800} = \cdot453 = \text{specific refraction}$$

$$\cdot453 \times 46 = 20\cdot84 = \text{molecular refraction}$$

Calculated from the above mean values for the elements we have—

$$\begin{array}{rcl} \text{C}_2 & = 2 \times 5 & = 10 \\ \text{H}_6 & = 6 \times 1\cdot3 & = 7\cdot8 \\ \text{O} & = 1 \times 3 & = 3 \\ \hline & & 20\cdot8 \end{array}$$

Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$ —

$$\begin{array}{l} \text{Density} = 1\cdot0495 \\ \text{Index of refraction} = 1\cdot3718 \\ \frac{n-1}{d} = \frac{\cdot3718}{1\cdot0495} = \cdot354 = \text{specific refraction} \\ \cdot354 \times 60 = 21\cdot24 \text{ (experimental)} \\ \begin{array}{rcl} \text{C}_2 & = 2 \times 5 & = 10 \\ \text{H}_4 & = 4 \times 1\cdot3 & = 5\cdot2 \\ \text{O}_2 & = 2 \times 3 & = 6 \\ \hline & & 21\cdot2 \text{ (theoretical)} \end{array} \end{array}$$

Acetic aldehyde—

$$\begin{array}{l} \text{Density} = \cdot798 \\ \text{Index of refraction} = 1\cdot331 \\ \frac{n-1}{d} = \frac{\cdot331}{\cdot798} = \cdot415 = \text{specific refraction} \\ \cdot415 \times 44 = 18\cdot26 \text{ (experimental)} \\ \begin{array}{rcl} \text{C}_2 & = 2 \times 5 & = 10\cdot0 \\ \text{H}_4 & = 4 \times 1\cdot3 & = 5\cdot2 \\ \text{O} & = 1 \times 3 & = 3\cdot0 \\ \hline & & 18\cdot2 \text{ (theoretical)} \end{array} \end{array}$$

Take three metamerides, as methyl acetate, ethyl formate, and propionic acid.

For the first, $\text{CH}_3(\text{C}_2\text{H}_3\text{O}_2)$, we have—

$$\text{Density} = \cdot 9039$$

$$\text{Index of refraction} = 1\cdot 36099$$

$$\frac{n-1}{d} = \frac{\cdot 36099}{\cdot 9039} = \cdot 398$$

$$\cdot 398 \times 74 = 29\cdot 45 \text{ (experimental)}$$

For the second, $\text{C}_2\text{H}_5(\text{CHO}_2)$, we have—

$$\text{Density} = \cdot 9064$$

$$\text{Index of refraction} = 1\cdot 3598$$

$$\frac{n-1}{d} = \frac{\cdot 3598}{\cdot 9064} = \cdot 397$$

$$\cdot 397 \times 74 = 29\cdot 38 \text{ (experimental)}$$

For the third, $\text{H}(\text{C}_3\text{H}_5\text{O}_2)$, we have—

$$\text{Density} = \cdot 9946$$

$$\text{Index of refraction} = 1\cdot 3866$$

$$\frac{n-1}{d} = \frac{\cdot 3866}{\cdot 9946} = \cdot 389$$

$$\cdot 389 \times 74 = 28\cdot 79 \text{ (experimental)}$$

$$\text{C}_3 = 3 \times 5 = 15$$

$$\text{H}_6 = 6 \times 1\cdot 3 = 7\cdot 8$$

$$\text{O}_2 = 2 \times 3 = 6$$

$$\text{For all three, } \quad \quad \quad 28\cdot 8 \text{ (theoretical)}$$

The close agreement between the calculated and the experimental results does not hold in every case, and in the case of unsaturated bodies especially the discrepancy is so very marked that we can only attribute the difference between the two to the structure of the molecule.

If we take the same two substances as we took for their molecular volumes—aniline and picoline, both with the empirical formula, $\text{C}_6\text{H}_7\text{N}$, we have for aniline—

Density = 1.0216

Index of refraction = 1.58629

$$\frac{n-1}{d} = \frac{.58629}{1.0216} = .574$$

$$.574 \times 93 = 52.38 \text{ (experimental)}$$

For picoline—

Density = .955

Index of refraction = 1.4965

$$\frac{n-1}{d} = \frac{.4965}{.955} = .52$$

$$.52 \times 93 = 48.36 \text{ (experimental)}$$

$$C_6 = 6 \times 5 = 30$$

$$H_7 = 7 \times 1.3 = 9.1$$

$$N = 1 \times 5.75 = 5.75$$

$$44.85 \text{ (theoretical)}$$

It is evident from these two examples that some modification of the values is necessary not only to explain the difference between the two, but also their difference from the theoretical one. Brühl, from the investigation of a large number of substances of very various constitution, has given the following values:—

Carbon,	5.00	2.365
Hydrogen,	1.30	1.103
Oxygen (O'), as in hydroxyl, .	2.80	1.506
Oxygen as in ether,	1.655
Oxygen (O''), as in carbonyl, .	3.40	2.328
Chlorine,	9.87	6.014
Bromine,	15.39	8.863
Iodine,	24.69	13.808
Nitrogen (N'), singly linked, .	5.75	2.76
Each double or ethylene linking,	2.30	1.836
Each treble or acetylene linking,	1.90	2.22

The first column has the values for the formula $\frac{n-1}{d}$, and the index of refraction for the red hydrogen ray. The values in the second are for the formula—

$$\frac{n^2 - 1}{n^2 + 2} \times \text{mol. volume} ; \text{ or } \frac{n^2 - 1}{n^2 + 2} \times \frac{\text{mol. wt.}}{d}$$

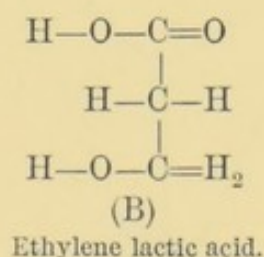
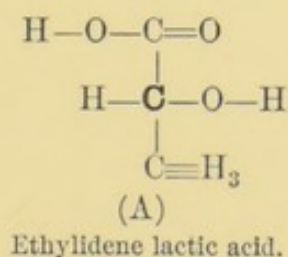
deduced independently by A. Lorentz and L. Lorenz from Maxwell's electromagnetic theory of light, and which has been shown by recent experiments to give results far superior to those of the older formula.

The above numbers indicate how the higher values in the unsaturated bodies are obtained, since for each double or treble linking an additional quantity must be added to that obtained from the carbon atoms alone.

One other interesting and important optical property is what is called circular polarisation. For details physical treatises must be consulted—suffice it to say, that if we take a Nicol's prism a beam of ordinary light transmitted through it emerges polarised, and will be transmitted practically without loss through another Nicol's prism held in an exactly similar position in the path of the ray ; but if it be turned through a right angle no light whatever will be transmitted. If we now place between these two prisms certain substances, both solid and liquid, light will pass through the second prism ; but if we turn it in the direction of the hands of a watch, or in the opposite direction, we find a point where we have again total extinction. Substances which behave thus to a beam of polarised light are said to polarise circularly. The Nicol's prism, through which the light first passes, is called the "polariser," and is generally fixed ; and the one next the eye the "analyser," and usually is capable of being rotated, and the angle of rotation measured. Substances which require the analyser to be rotated in the direction of the hands of a watch are said to be "dextro-rotatory," and those in the opposite direction,

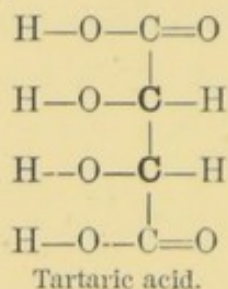
“lævo-rotatory.” In the case of solids, such as rock crystal, we have both kinds, as well as one which is inactive. Its rotatory power is plainly due to the arrangement of the molecules in the solid crystal, and can be imitated by means of mica plates suitably arranged, as shown by Sohncke. The forms of the crystals themselves differ in such a way, that before testing with polarised light one can tell whether the action will be dextro- or lævo-rotatory. Their relations to one another are those of an object to its reflection in a mirror, or that of the right and left hands. When we dissolve such solids in water this action on light ceases. Many liquids, however, exert this action powerfully, and many solids in solution do the same. In this case, then, the property must be due to the arrangement of the atoms in the molecule, since they are in motion in all directions; but in the solids which give inactive solutions it must be due to the arrangement of the molecules when built up to form the solid.

Almost all the solids whose solutions are active are inactive in the solid form. All the liquids which possess this property are either themselves compounds of carbon or solutions of them. Their number is relatively small, but all contain what has been termed an “asymmetric” carbon atom—that is, a carbon atom to which are attached four different groups or radicals. If we take the two lactic acids, we have—



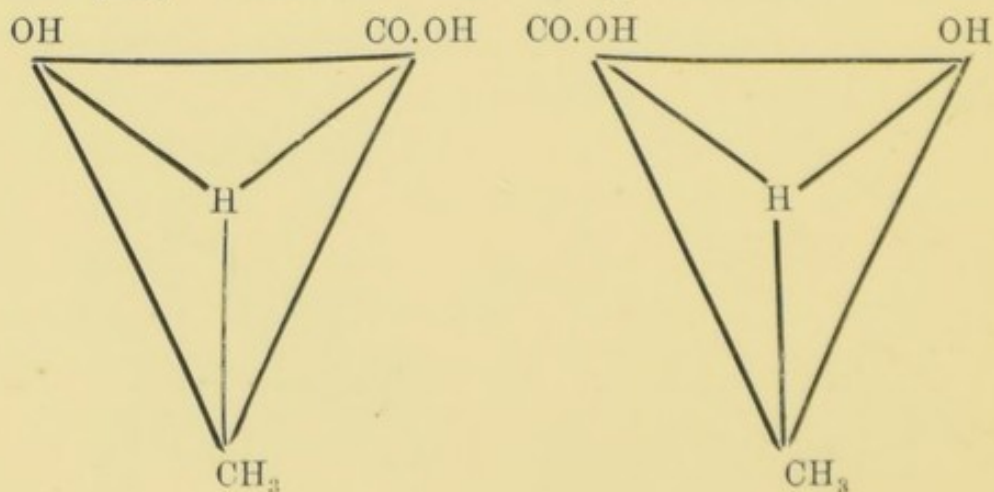
A has an “asymmetric” carbon atom, for it has the

four different groups, (H)', (OH)', (CH₃)', (CO.OH)' attached to it. B has, however, no such atom. A is active, B is inactive. Again, tartaric acid has the formula—



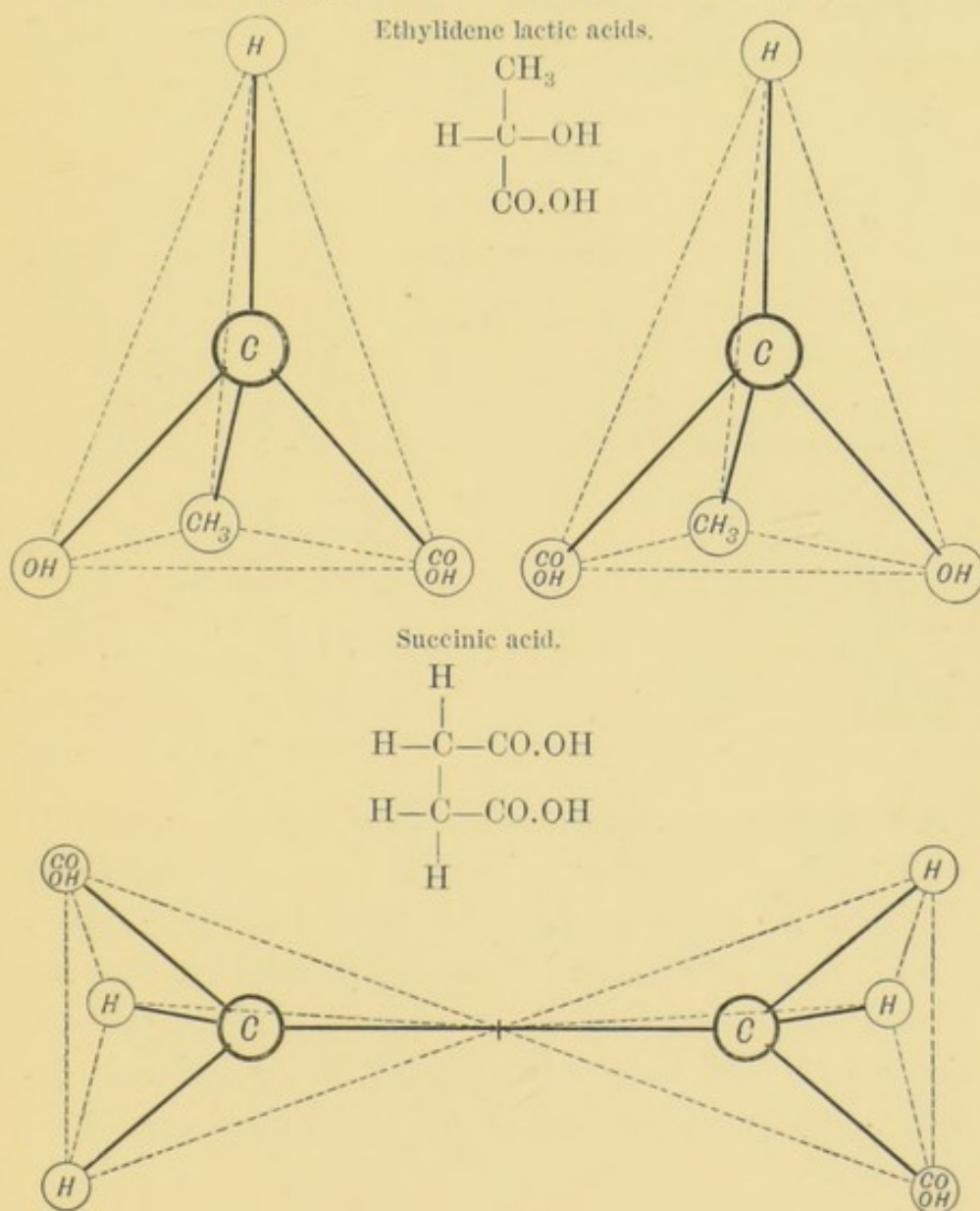
It has two asymmetric carbon atoms, and may give, then, an active or inactive modification. We actually know (1) a *dextro*-tartaric acid; (2) an *equally lævo*-tartaric acid; (3) racemic acid, which is a compound of these two, and can be separated into them; (4) an inactive tartaric acid, which is not separable into the two acids.

These are explained by an ingenious theory due to Le Bel and van't Hoff. If we imagine a carbon atom at the centre of a tetrahedron, and united to four different groups, one being situated at each point, we can arrange them so that we have two structures which are to one another as an object and its mirror image, as may be readily seen if we look down on the figures, when the carbon atom will appear as situated immediately below the apex, and need not be here represented—

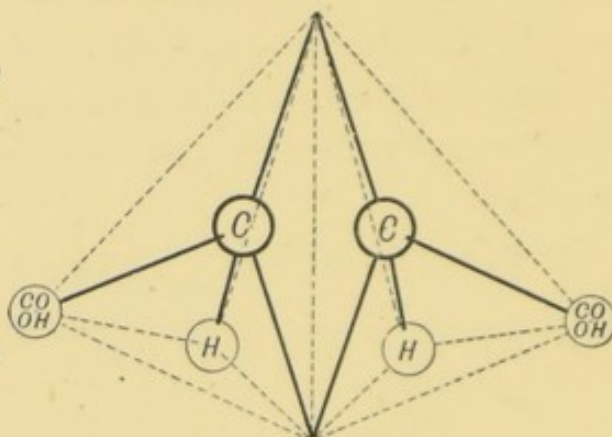
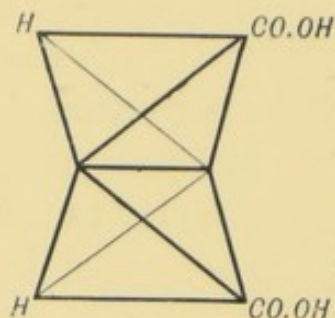
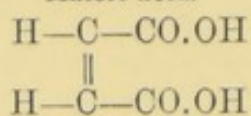


These figures would represent two possible *physical* isomers of lactic (ethylidene) acid. The isomerism of fumaric and maleic acids, and the transformation of the one into the other, the formation of fumaric anhydride, &c., can easily be explained on this theory, for further details regarding which more advanced books must be consulted.

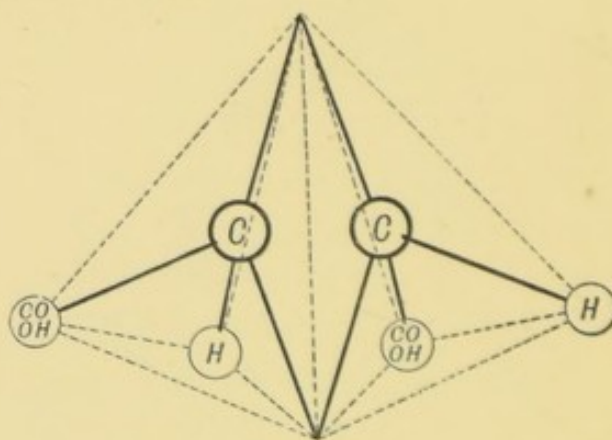
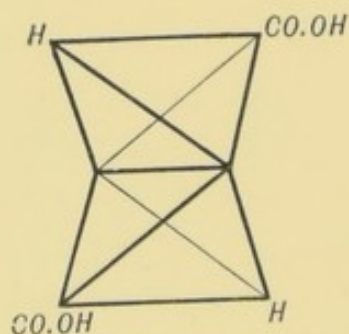
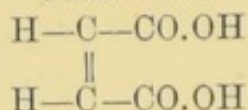
The following typical bodies may be thus represented:—



Maleic acid.



Fumaric acid.



Attempts to connect the colour of inorganic compounds with their composition have not been very successful, although we have made much more definite progress with organic substances. Carnelley pointed out that the addition of the electro-negative element tended to darken the colour, and that this changed in the order of refrangibility, white and black being the extremes, as we see from

Cuprous chloride, . . .	Cu_2Cl_2 ,	white.
Cupric chloride, . . .	CuCl_2 ,	green or blue.
Potassium ferrocyanide, . . .	$\text{K}_4\text{Fe}(\text{CN})_6$,	yellow.
Potassium ferricyanide, . . .	$\text{K}_3\text{Fe}(\text{CN})_6$,	red.
Potassium manganate, . . .	K_2MnO_4 ,	green.
Potassium permanganate, . . .	KMnO_4 ,	purple-red.
Manganous oxide, . . .	MnO ,	pale green.
Trimanganic tetroxide, . . .	Mn_3O_4 ,	reddish-brown.
Manganese dioxide, . . .	MnO_2 ,	black.
Potassium chromate, . . .	K_2CrO_4 ,	yellow.
Potassium bichromate, . . .	$\text{K}_2\text{Cr}_2\text{O}_7$,	orange-red.

In many cases we have just the reverse, as

Mercuric oxide, . . .	HgO ,	red or yellow.
Mercurous oxide, . . .	Hg_2O ,	black.
Stannic sulphide, . . .	SnS_2 ,	yellow.
Stannous sulphide, . . .	SnS ,	dark brown.
Orpiment, . . .	As_2S_3 ,	yellow.
Realgar, . . .	As_2S_2 ,	red.
Ferrous chloride, . . .	FeCl_2 ,	greyish-white.
Ferric chloride, . . .	Fe_2Cl_6 ,	black.

CHAPTER IX.

THERMO-CHEMISTRY.

IN our ordinary chemical equations some very important parts of the phenomena occurring during the reaction or reactions which they represent are entirely ignored. In the majority of reactions which take place there is an evolution of energy, which usually takes the form of heat. We may in many cases, however, have it as electrical separation. One of our fundamental chemical laws is that matter is uncreatable and indestructible. We have another also which is equally true, and that is, that the energy of an isolated system is always the same, energy like matter being uncreatable and indestructible. Energy, or the power of doing work, is fundamentally of two kinds—*kinetic* and *potential*. The former is that due to matter in actual motion, the latter to the position or arrangement of the matter in the system. These may change into one another, but the sum remains the same. A very simple case is that of a pendulum swinging. At each side it *stops* at its highest point, then returns. When it stops all its energy is due to its position, and is in the form of potential energy, but at its lowest point it is moving with its maximum velocity, and has all its energy as kinetic energy; but this is sufficient to raise it again to a height equal to that from which it started, whilst at intermediate points its energy is of both kinds.

We have seen that hot bodies consist of particles moving with immense velocity, and their energy is therefore kinetic. If we take a system consisting of carbon and oxygen, these two bodies may be compared to a weight raised from the earth. When the weight is allowed to fall, the potential energy due to the relative position of the earth and the weight is converted into heat. In a somewhat similar way the atoms of the carbon and the oxygen, coming together to form a compound, generate a large amount of heat. A system consisting of carbon and oxygen in the elementary condition possesses potential energy, which, when these elements are allowed to combine, is converted into heat. But to raise a weight from the earth to the height from which it has fallen, an amount of heat, or other form of energy equal to that which it produced on falling, is required; so when two elements unite to form a compound with an evolution of heat the same amount of heat is required to decompose the compound formed, and restore the elements to their original condition. This was recognised by Lavoisier, and clearly enunciated by him, and has been completely confirmed by numberless experiments. It need hardly be pointed out that it is a necessary consequence of the modern doctrine of energy. In many cases we can measure the energy set free on the combination of two elements directly; but we have many cases, such as gold and oxygen, combined to form auric oxide, or chlorine and nitrogen to form nitrogen chloride, where we have the free elements exhibiting no tendency to combine, but quite the reverse, so much so, that when combined, their readiness to separate is very marked. We thus get bodies with various degrees of stability,

and may define stable bodies as those which evolve much heat in their formation, and unstable bodies those which absorb much when they are formed. Those which have given out much heat when formed require an equivalent amount of heat or other form of energy to decompose them ; but those which have absorbed heat require not only no external energy to be supplied to them, but are ready to give energy on their decomposition. In the majority of chemical reactions heat is given out, and, as a rule, when several reactions are possible, that which tends to produce most heat is that which takes place. Any reaction in which heat is given out is said to be *exothermic*, and when heat is absorbed it is called *endothermic*. Various methods are adopted to determine the heats of formation of substances. They may be determined from the direct union of the elements to form the compound without the intervention of solution. For example, in determining the heat evolved in the formation of water from hydrogen and oxygen, the two gases are supplied at carefully regulated rates and burnt in a metallic vessel, surrounded by a large quantity of water, the mass of which, along with the water equivalent of vessel, thermometer, and stirrer, is accurately known. The rise in temperature, multiplied by the mass in grams, gives the amount of heat generated by the combustion of the known amount of hydrogen and oxygen supplied ; or they may be mixed in a stronger metal vessel, immersed in water, and exploded. The reactions in solution are usually carried out with very dilute solutions, and the reacting masses are very small compared with the total masses experimented upon.

The measurements made by different experimenters in thermal chemistry generally are not nearly so concordant as those in other branches, and this arises largely from the fact that the rises in temperature are small, and have to be multiplied by large masses, so that an error of only $\frac{1}{100}$ of a degree in reading produces a serious error in the result. In dealing with very dilute solutions, it is often assumed that the specific heat of such is equal to that of the water they contain, and this is only approximately true. In tables of heats of combination, the data given are usually for the ordinary temperature of the laboratory (18° C.), unless otherwise specified. It is also always necessary carefully to bear in mind the heat due to any physical change, and to note the physical state of the components and that of the compound formed. One of the most fundamental determinations is the heat evolved on the union of hydrogen with oxygen to form water. Thomsen gives the following experiments :—

	I.	II.	III.
Total mass	= 2460	2460	2464
Rise in temperature	= $3^{\circ}\cdot282$	$12^{\circ}\cdot321$	$13^{\circ}\cdot508$
Water produced	= $2\cdot129$	$7\cdot989$	$8\cdot810$
Heat evolved	= 8074	30309	33284
Corrections	= 15	86	112
	<hr/> 8089	<hr/> 30395	<hr/> 33396
For 18 grams	= 68388	68467	68231

giving as a mean the value 68357 units of heat evolved by the combination of 2 grams of hydrogen with 16 grams of oxygen to form 18 grams of water. The results of various experimenters for the same, which we usually write (H_2O), the bodies uniting (or often only supposed

to unite) being separated by a comma, are the following :—

(H ₂ ,O)	=	69486 (Dulong).
„	=	69584 (Hess).
„	=	69332 (Grassi).
„	=	68433 (Andrews).
„	=	68924 (Favre and Silbermann).
„	=	68357 (Thomsen).

If we take O = 16, H = 1·0025, then for (H₂,O) or the formation of 18·005 grams of water = 68376; and if O = 15·96 and H = 1, (H₂,O) or the formation of 17·96 grams of water = 68207. If we correct this to 0° C., this becomes—

68346 (Thomsen).
68252 (Schuller and Wartha).
68461 (Than).

Similarly for hydrochloric acid. The production of 13·08 grams of hydrochloric acid from its elements raised the temperature of 2460 grams of water 3°·205. Whence for 1 gram we get 602·1, and for (H,Cl) or the formation of 36·5 grams of hydrochloric acid *gas* = 21976. The mean of four experiments gave the value for (H,Cl) = 22001.

To determine the heat evolved by the formation of a dilute solution from gaseous hydrochloric acid, the gas carefully dried, was passed into water in a glass flask, when it was found that for the solution of 36·5 grams of gaseous hydrochloric acid in much water (Aq)

17279
17351
17311

∴ as a mean, 17314 units of heat were evolved.

We have then—

$$\begin{aligned} (\text{H}, \text{Cl}) &= 22001 \\ (\text{HCl}, \text{Aq}) &= 17314 \\ \therefore (\text{H}, \text{Cl}, \text{Aq}) &= 39315 \text{ heat units.} \end{aligned}$$

In passing from any initial condition to any final condition, the heat evolved (or absorbed) is a perfectly definite quantity which is quite independent of the number and sequence of these changes. It depends solely on the initial and the final states. This law is of very great importance in determining many heats of combination which cannot be estimated directly.

In many elements we have allotropic modifications, and we find that the heat evolved on their combustion in oxygen depends on the condition of the body burnt. We must regard that form which gives the least amount of heat on combustion as the most stable form. For example :—

1 gram of diamond burnt to $3\frac{2}{3}$ grams of carbon dioxide	
gives out,	7770
„ graphite	7797
„ charcoal	8080

Or for 12 grams—

Diamond,	93240
Graphite (natural),	93560
Charcoal,	96960

We may regard charcoal burning to carbon dioxide as taking place in two steps—

12 grams charcoal becoming 12 grams graphite	= 3400
12 grams graphite burning to 44 grams carbon dioxide	= 93560
\therefore 12 grams charcoal burning to 44 grams carbon dioxide	= 96960

In the same way the change of 31 grams of yellow

phosphorus into 31 grams of red phosphorus (cryst.) gives 19600 units of heat.

Carbon, say in the form of charcoal (solid), may be burnt into carbon dioxide (gas) in two stages, we might even say three stages:—

1. Solid carbon to gaseous carbon.
2. Gaseous carbon to carbon monoxide.
3. Gaseous carbon monoxide to gaseous carbon dioxide.

The total for 1, 2, and 3 is 96960 for 12 grams of charcoal burning to 44 grams of carbon dioxide. Now, 28 grams of carbon monoxide in burning to 44 grams of the dioxide give 67960, leaving thus for $\left(\begin{smallmatrix} \text{C} \\ \text{solid} \end{smallmatrix}, \text{O}\right) = 96960 - 67960 = 29000$. In very many cases the heat of combination of a dioxide is almost exactly double that of the monoxide, so a large amount of heat seems to be absorbed in changing solid carbon to gaseous carbon. So that we might write—

1. = - 38960 C (solid) to C (gas)
2. = + 67960 C (gas) to CO = (C, O)
3. = + 67960 CO to CO₂ = (CO, O)

$$1, 2, \text{ and } 3 = 96960 = \left(\begin{smallmatrix} \text{C} \\ \text{solid} \end{smallmatrix}, \text{O}_2\right)$$

$$(\text{Cu}_2, \text{O}) = 39976 \quad (\text{Cu}_2, \text{O}_2) = 76580$$

$$\therefore (\text{Cu}_2\text{O}, \text{O}) = 36604$$

and

$$\text{Sn, O} = 69780 \quad (\text{Sn, O}_2) = 135360$$

$$\therefore \text{SnO, O} = 65580$$

Taking the three hydrocarbons, acetylene, C₂H₂, ethylene, C₂H₄, and ethane, C₂H₆, we have the heat of combustion of 26 grams of acetylene = (C₂H₂, O₅) = 310450.

Now,

$$\begin{array}{r} (\text{C}_2, \text{O}_4) = 193920 \\ (\text{H}_2, \text{O}) = 68357 \\ \hline \end{array}$$

$$\therefore 2(\text{C}, \text{O}_2) + (\text{H}_2, \text{O}) = 262277$$

That is to say, we get more heat by burning the compound than by burning the same weights of its components as elements. 48173 units of heat must, therefore, be absorbed by the union of 24 grams of solid carbon with 2 grams of hydrogen to form 26 grams of gaseous acetylene, for we have

$$\begin{array}{r} (\text{C}_2, \text{H}_2) = x \\ (\text{C}_2\text{H}_2, \text{O}_5) = 310450 \\ (\text{C}_2, \text{H}_2, \text{O}_5) = 262277 = 310450 + x \\ \hline \end{array}$$

$$\therefore (\text{C}_2, \text{H}_2) = - 48173 = x$$

Similarly, 28 grams of ethylene, on burning to carbon dioxide and water, give 333350; but 24 grams carbon and 4 grams hydrogen give

$$\begin{array}{r} 193920 + 136714 = 330634 \\ \therefore (\text{C}_2, \text{H}_4) = 330634 - 333350 = - 2716 \end{array}$$

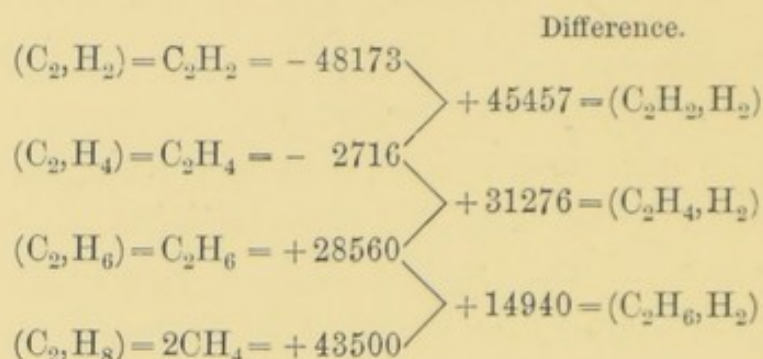
and for ethane—

$$\begin{array}{r} (\text{C}_2\text{H}_6, \text{O}_7) = 370440 \\ \hline (\text{C}_2, \text{O}_4) = 193920 \\ (\text{H}_6, \text{O}_3) = 205080 \\ \hline (\text{C}_2, \text{H}_6, \text{O}_7) = 399000 \\ (\text{C}_2\text{H}_6, \text{O}_7) = 370440 \\ \hline (\text{C}_2, \text{H}_6) = + 28560 \end{array}$$

For methane we have—

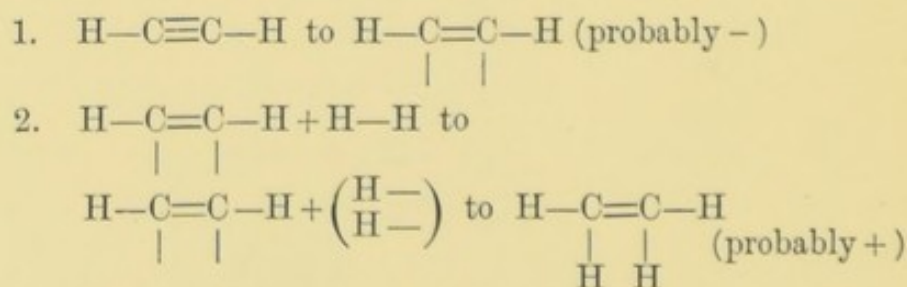
$$\begin{array}{r} (\text{CH}_4, \text{O}_4) = 211930 \\ \hline (\text{C}, \text{O}_2) = 96960 \\ (\text{H}_4, \text{O}_2) = 136420 \\ \hline \therefore (\text{C}, \text{O}_2) + (\text{H}_4, \text{O}_2) = 233680 \\ \therefore (\text{C}, \text{H}_4) = + 21750 \end{array}$$

We have, therefore, for the values—



These differences are almost in the ratios of 3 : 2 : 1, and a most interesting paper of a speculative nature by Thomsen is based on these and many similar data with regard to the heat relations of the union of one atom of carbon with another singly, doubly, and trebly. It is quite evident, as in the case of the oxides, that the formation of the simplest *gaseous* compound from *solid* carbon involves a very large absorption of heat; but that after we have obtained a gaseous compound, the successive additions of hydrogen each give large evolutions of heat, which tend to become much smaller as the carbon becomes more nearly saturated. It must be observed, however, that heat evolution is due to two actions—the loosening of the combination of the carbon atoms (probably -), and the combination of the hydrogen in its place (probably +).

Going from acetylene to ethylene, we may have—



It may be as well here to point out that when we say

that the value of $(H, Cl) = 22001$, we are not strictly correct; what we ought to write is $(H_2, Cl_2) = 44002$, and the heat evolution due to the formation of hydrochloric acid from gaseous hydrogen and chlorine is only the excess of $2(H, Cl)$ over $(H, H) + (Cl, Cl)$; that is to say, that before we can form two molecules of hydrochloric acid we have to decompose the hydrogen and chlorine molecules into atoms and this involves a very large absorption of heat, probably many times as great as the quantity we measure. So that $(H_2, Cl_2) = 2HCl$ may be written in three steps:—

1. H_2 to $H + H$ = a large - quantity.
2. Cl_2 to $Cl + Cl$ = „ „
3. $(H + H), (Cl + Cl)$ to $2(HCl) = +44002$ more than (1) and (2) together.

Several other compounds of carbon are worthy of individual mention. First, we will take carbon disulphide, CS_2 , which is usually prepared by the combustion of carbon in sulphur vapour, but this is very unlike the corresponding combustion of carbon in oxygen to carbon dioxide, for the latter, when once started, goes on with great vigour and evolution of much heat, but the latter requires the aid of external heat to enable the combination to go on; and we find heat is largely absorbed.

$$\begin{aligned} (C, S_2) &= -26010 \text{ for gaseous carbon disulphide.} \\ „ &= -19610 \text{ for liquid „ „} \end{aligned}$$

The heat of formation of 76 grams of carbon disulphide is determined thus—

$$\begin{array}{rcl} & (CS_2, O_6) & = 265130 \\ \text{but} & (C, O_2) & = 96960 \\ \text{and} & 2(S, O_2) & = 142160 \\ & \hline \therefore (C, O_2) + 2(S, O_2) & = 239120 \end{array}$$

$$\therefore (C, S_2) = 239120 - 265130 = -26010$$

$$CS_2 \text{ gas to } CS_2 \text{ liquid} = +6400$$

$$\therefore (C, S_2) \text{ to } CS_2 \text{ liquid} = -26010 + 6400 = -19610$$

Cyanogen is similarly formed with a large absorption of heat; for, on burning 52 grams of it an evolution of 259620 heat units was obtained. This represents $(C_2N_2, O_4) = 2(C, O_2) - (C_2, N_2)$, that is, the heat of formation of carbon dioxide minus the heat of formation of cyanogen (or plus the heat of decomposition of cyanogen).

$$2(C, O_2) = 193920$$

$$\therefore (C_2, N_2) = 193920 - 259620 = -65700$$

Acetylene, carbon disulphide, and cyanogen ought all to be readily decomposed into their elements explosively, and with the evolution of much heat; and this has been shown to be the case by Berthelot with regard to acetylene and cyanogen, and by Thorpe for carbon disulphide. The detonation of a little mercuric fulminate in a tube filled with carbon disulphide vapour causes an explosion of the vapour and its separation into its elements.

Before leaving the compounds of carbon we will consider one or two substances used as fuels and containing the three elements, carbon, hydrogen, and oxygen.

1. Ethyl alcohol, C_2H_6O , of which we have the heat of combustion = 340530, which is the heat evolved in the change (C_2H_6O, O_6) to $2CO_2 + 3H_2O$; but

$$2(C, O_2) + 3(H_2, O) = 193920 + 205080 = 399000$$

$$\therefore \text{heat of formation} = 399000 - 340530 = +58470 = (C_2, H_6, O)$$

2. Cellulose, $C_6H_{10}O_5$.

$(C_6H_{10}O_5, O_{12}) = 6CO_2 + 5H_2O$, with evolution of 721000 heat units.

$$6(C, O_2) + 5(H_2, O) = 923560$$

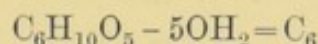
$$\therefore (C_6, H_{10}, O_5) = 923560 - 721000 = +202560$$

Now, the ordinary rule given for calculating the heat-giving power of a fuel from its composition is to subtract the oxygen with an equivalent amount of hydrogen (and carbon if necessary), and take the remainder as that which alone will give any heat on combustion, that is, for ethyl alcohol, $C_2H_6O - OH_2 = C_2H_4$, we are to assume that 24 parts of carbon + 4 parts of hydrogen will give the same amount of heat on combustion as 46 parts of ethyl alcohol.

$$\begin{array}{rcl} 46 \text{ parts of ethyl alcohol give} & . & 340530 \\ 24 \text{ parts of carbon} & \} & 193920 \\ + 4 \text{ parts of hydrogen} & \} \text{ give } + 136720 & \} = 330640 \end{array}$$

Hence we get really more heat to the extent of 9890 units than the practical rule indicates.

For cellulose, again,



that is, 162 parts of cellulose are assumed to be equal in heat-giving power to 72 parts of carbon.

$$\begin{array}{rcl} 162 \text{ parts of cellulose on combustion give} & 721000 \\ 72 \text{ parts of charcoal} & ,, & 581760 \end{array}$$

$$\text{Excess over practical rule} = 139240$$

the rule giving in this case only about $\frac{1}{16}$ ths of the amount really available.

We have already seen how the heat of formation of hydrochloric acid has been determined. It has been also stated more than once that the evolution of heat given by hydrogen and chlorine uniting is greater than that of hydrogen and bromine, and this in turn is greater than that of hydrogen and iodine. Now, by passing chlorine into solutions of hydrobromic and hydriodic acids, we get bromine and iodine set free respectively,

and hydrochloric acid formed. We may, then, use this reaction for determining the values of (H,Br) and (H,I) becoming HBr and HI, these two values not being obtainable directly :—

$$\begin{aligned}(\text{HBrAq, Cl}) &= \text{HClAq} + \text{BrAq} + 11478 \\,, &= (\text{H, Cl, Aq}) - (\text{H, BrAq})\end{aligned}$$

To get the hydrogen for the chlorine we must decompose the hydrobromic acid ; the bromine will remain dissolved and the hydrogen and chlorine will unite and evolve 22001 units, then solution in water gives a further evolution of 17314, in all 39315 units. We have only, however, an evolution from 11478 units, from which must be subtracted 19936, the heat of solution of hydrobromic acid.

Practically, however, solution of potassium bromide is used instead of hydrobromic acid, and we have really a far more complicated series of reactions to consider.

The heat of formation of solution of potassium chloride from potassium, chlorine and water, or (K,Cl,Aq), is got from the series of reactions following :—

$$\begin{aligned}(\text{K, O, H, Aq}) + (\text{H, Cl, Aq}) + (\text{KOHAq, HCl, Aq}) - (\text{H}_2\text{O}) &= (\text{K, Cl, Aq}) \\ \text{for } (\text{K, O, H}) + (\text{H, Cl}) &= (\text{K, Cl}) + (\text{H, O, H}) + \text{heat.}\end{aligned}$$

Some of the heat is due to the (K,Cl), some to the (H₂O). A certain amount of heat is used up in forming the solution of the solid potassium chloride in water—

$$(\text{KCl, Aq}) \text{ becoming } (\text{KClAq}) = -4440$$

If, then, we compare the formation of potassium bromide in the same way, we have—

$$\begin{aligned}(\text{K, O, H, Aq}) + (\text{H, Br, Aq}) + (\text{KOHAq, HBrAq}) - (\text{H}_2\text{O}) &= (\text{K, Br, Aq}) \\ (\text{K, O, H, Aq}) + (\text{H, Cl, Aq}) + (\text{KOHAq, HClAq}) - (\text{H}_2\text{O}) &= (\text{K, Cl, Aq})\end{aligned}$$

The larger evolution of heat is due to the lower equation, and it is evident that in each we have several similar

terms. The first term is identical. The second term is that in which the chief difference comes in. The third term is the same; this is proved by experiment, being equal in each to 13740 units. The fourth term is again identical in each.

From these it follows that by the reaction of chlorine on potassium bromide in solution, we get exactly the same evolution of heat as if we had used hydrobromic acid in solution.

$$\begin{aligned} \therefore (K, Cl, Aq) - (K, BrAq) &= (H, Cl, Aq) - (H, BrAq) = 11478 \\ \text{but } (H, Cl, Aq) &= 39315 \\ &\quad 11478 \\ \hline \therefore (H, BrAq) &= 27837 \end{aligned}$$

This is less than (H, Br, Aq) by the value for (Br, Aq) , the heat given out by 80 grams of liquid bromine dissolving in much water, which is 539 heat units.

$$\begin{aligned} \therefore (H, Br, Aq) &= 27837 + 539 = 28376 \\ \text{but } (HBr, Aq) &= 19936 \\ \hline \therefore (H, Br) &= 8440 \end{aligned}$$

The bromine is here taken as liquid. The value for (H, Br) , both gaseous at about 60° C. , is 12300. Similarly for hydriodic acid, which we will write somewhat differently:—

$$\begin{aligned} (K, O, H, Aq) + (H, Cl, Aq) + (KOH Aq, HCl Aq) - (H_2, O) &= (K, Cl, Aq) \\ \text{Identical} \quad 39315 \quad 13740 \quad \text{identical} \quad \text{difference} \\ &= 26209 \\ (K, O, H, Aq) + (H, I, Aq) + (KOH Aq, HCl Aq) - (H_2, O) &= (K, I, Aq) \\ &\quad x \quad 13675 \\ 39315 + 13740 &= 13675 + 26209 + (H, I, Aq) \\ 53055 &= 39884 + (H, I, Aq) \\ 13171 &= (H, I, Aq) \\ \text{but } (HI, Aq) &= 19207 \\ \hline \therefore (H, I) &= - 6036 \end{aligned}$$

Hydriodic acid is therefore an unstable body, and separates into its elements with an evolution of heat, but its dilute solution is perfectly stable (in absence of air or oxygen). It may be prepared by the action of hydrosulphuric acid on iodine and water, and this reaction enables us to determine the heat of combination of hydrogen and sulphur to form hydrosulphuric acid gas. The ordinary equation is

$$\begin{aligned}
 &2\text{H}_2\text{S} + 2\text{I}_2 = 4\text{HI} + \text{S}_2 \\
 &(\text{I}_2, \text{Aq}, \text{H}_2\text{S}) = 2(\text{H}, \text{I}, \text{Aq}) - (\text{H}_2, \text{S}) = 21600 \\
 \text{but} \quad &2(\text{H}, \text{I}, \text{Aq}) = 2(13171) = 26342 \\
 &26342 - (\text{H}_2, \text{S}) = 21600 \\
 \therefore &4740 = (\text{H}_2, \text{S})
 \end{aligned}$$

That is the formation of 34 grams of gaseous hydrosulphuric acid from 2 grams of hydrogen and 32 grams of white sulphur (precipitated) results in the evolution of 4740 heat units; and as 34 grams of hydrosulphuric acid dissolving in water give 4560 heat units, we get in all for

$$(\text{H}_2, \text{S}, \text{Aq}) = 4740 + 4560 = 9300$$

The above reaction of hydrosulphuric acid on iodine requires the presence of water; dry hydrosulphuric acid has no action on dry iodine. If we pass the hydrosulphuric acid gas into water containing much iodine, we find that after a time we get no further reaction. Hydriodic acid gas passed into very much water gives out 19207 heat units, but when the solution becomes somewhat concentrated a much smaller evolution is produced; this becomes less and less, and when it falls to about 15336, we have just as much heat formed as is required to decompose the hydrosulphuric acid in aqueous solution. This, we saw above, was 9300. The total heat due to

$$(\text{H}, \text{I}) + (\text{HI}, \text{Aq}) - (\text{H}_2, \text{S}, \text{Aq})$$

at the beginning is equal to an evolution of

$$-6036 + 19207 - 9300 = 3871 \text{ units}$$

but when the value of $(\text{HI}, \text{Aq} + n\text{HI})$ falls to 15336, we have

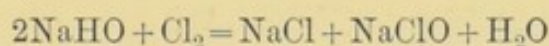
$$-6036 + 15336 - 9300 = 0$$

The action must stop unless energy from an external source is supplied. The reaction ceases when about 10 per cent. of hydriodic acid is in solution.

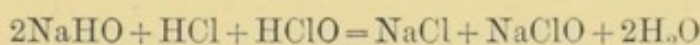
Another very good example indicating the methods employed and the precision obtained by different reactions by the same experimenter is hypochlorous acid.

On passing chlorine into sodium hydrate solution, we obtain sodium chloride and sodium hypochlorite in solution. The same result would have been brought about by dividing the soda into two equal parts, and adding equivalent amounts of hydrochloric and hypochlorous acids. The heat evolved in each process will be very different however, and from this difference we can calculate the quantity we desire.

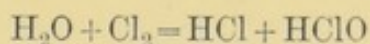
In ordinary notation we write the one reaction—



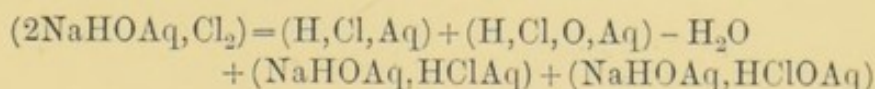
The other—



The second reaction flows from the first, if we assume that the chlorine decomposes a molecule of water to form the two acids thus—



Resolving the reaction of chlorine on sodium hydrate solution into factors, we have—



Now,

$$\begin{array}{rcl} (\text{NaHOAq}, \text{Cl}_2) & = & 24647 \\ (\text{NaHOAq}, \text{HClAq}) & = & 13740 \\ (\text{NaHOAq}, \text{HClOAq}) & = & 9976 \end{array} \quad \begin{array}{l} \text{H, Cl, Aq} = 39315 \\ (\text{H}_2, \text{O}) = 68357 \end{array}$$

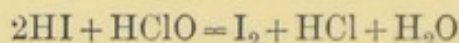
The only unknown quantity is therefore $(\text{H, Cl, O, Aq}) = x$.

$$24647 = 39315 + x - 68357 + 13740 + 9976$$

$$24647 = x - 5326$$

$$29973 = x = (\text{H, Cl, O, Aq})$$

The other reaction employed is represented by the equation—



We decompose hydriodic and hypochlorous acids, and form free iodine, hydrochloric acid and water with a large evolution of heat. Breaking it up into its reactions, we have—

$$(\text{HClOAq}, 2\text{HIAq}) = (\text{H, Cl, Aq}) + (\text{H}_2, \text{O}) - (\text{H, O, Cl, Aq}) - 2(\text{H, I, Aq})$$

Now,

$$(\text{HClOAq}, 2\text{HIAq}) = 51435$$

whence

$$51435 = 39315 + 68357 - x - 26342$$

$$51435 = 81330 - x$$

$$\therefore 29895 = x = (\text{H, O, Cl, Aq})$$

The mean value is 29934 for (H, O, Cl, Aq) . To deduce from this the heat of formation of the anhydride Cl_2O , we must know the heat evolved by its solution in much water—

$$\begin{array}{rcl} \therefore (\text{Cl}_2, \text{O}) & = & x \\ (\text{Cl}_2\text{O}, \text{Aq}) & = & 9440 \\ (\text{H}_2, \text{O}) & = & 68357 \end{array}$$

$$\begin{array}{rcl} \text{give} & 2(\text{H, Cl, O, Aq}) & = 2(29934) = x + 9440 + 68357 \\ & & 59868 = x + 77797 \end{array}$$

$$\therefore (\text{Cl}_2, \text{O}) = -17929 = x$$

When an acid and a base neutralise one another, giving rise to a salt and water, we have, as has long been recognised, a large evolution of heat. The amount of heat thus produced when using equivalent quantities of various acids and bases is by no means the same, although the variations are by no means so great as one might naturally expect from the way terms such as "strong acid," "weak acid," "strong base," &c., are freely employed. It was maintained by some chemists that the variations in the evolution of heat were due to the acid alone, and by others that it was the base which caused them, whereas it really depends on both.

To study the phenomena properly, we must use solutions so dilute that there will be no evolution nor absorption of heat on diluting them still further with a fair amount of water at the same temperature, because we will have water resulting from the reaction which will mix with the water in which the acid and base are dissolved. The strength used by Thomsen is 200 molecules of water to 1 equivalent of the acid or base, which for soda will be $\text{NaOH} = 23 + 16 + 1 = 40$ grams in $200 \text{ H}_2\text{O} = 200 \times (16 + 2) = 3600$ grams of water; for hydrochloric acid, $\text{HCl} = 1 + 35.5 = 36.5$ grams in 3600 grams of water; and for sulphuric acid, being dibasic, we must have $\text{H}_2\text{SO}_4 = 2 + 32 + 64 = 98$ grams in $2 \times 3600 = 7200$ grams of water, or $\frac{98}{2} = 49$ grams in 3600 grams of water.

With such solutions we may determine on thermal grounds what the basicity of an acid is, *provided we know its molecular weight*.

If we take such a solution as above described, con-

taining 98 grams of sulphuric acid, and add the base (say soda) in equivalent quantities, for each equivalent of hydrogen replaced in the acid we ought to have an evolution of heat. It does not necessarily follow, however, that the first and second equivalents of soda added thus will produce the same amount of heat. How these are related we shall see better by examples. In many cases we have also much smaller evolutions, and sometimes absorptions of heat, on adding excess of the acid or the base to the solution containing the normal salt. Many acids behave in a way we would not expect, judging from their general chemical reactions.

I.—*Monobasic Acids.*

Name of Acid.	Q.	(NaOHAq,QAq).
Hydrofluoric acid, . . .	H.F	16270
Hydrochloric acid, . . .	H.Cl	13740
Hydrobromic acid, . . .	H.Br	13750
Hydriodic acid, . . .	H.I	13680
Hydrosulphuric acid, . .	H.SH	7740
Hypochlorous acid, . . .	H.ClO	9980
Chloric acid,	H.ClO ₃	13760
Nitric acid,	H.NO ₃	13680

II.—*Dibasic Acids.*

Name of Acid.	Q.	(2NaOHAq,QAq).
Hydrofluosilicic acid, . .	H ₂ .SiF ₆	26620
Hydrochloroplatinic acid,	H ₂ .PtCl ₆	27220
Sulphuric acid,	H ₂ .SO ₄	31380
Chromic acid,	H ₂ .CrO ₄	24720
Periodic acid,	H ₂ .IH ₃ O ₆	26590
Arsenious acid,	H ₂ .As ₂ O ₄	13780
Phosphorous acid,	H ₂ .PHO ₃	28450
Carbonic acid,	H ₂ .CO ₃	20180
Silicic acid,	H ₂ .SiO ₃	5230

III.—*Tribasic Acids.*

Name of Acid.	Q.	(3NaOHAq,QAq).
Phosphoric acid, . . .	$H_3.PO_4$	34030
Arsenic acid, . . .	$H_3.AsO_4$	35920

IV.—*Tetrabasic Acid.*

Name of Acid.	Q.	(4NaOHAq,QAq).
Pyrophosphoric acid, .	$H_4.P_2O_7$	52740

The above tables show the heat evolved on neutralising the acids with sodium hydrate according to Thomsen's experiments. We must now look at the results of his experiments on adding the soda in single equivalents, or sometimes in fractions of an equivalent.

Name of Acid.	Q.	n.	(nNaOHAq,QAq).	m.	NaOHAq,mQAq.
<i>Monobasic Acids—</i>					
Hydrofluoric acid, }	H.F	{ 1	16272	1	16272
		{ 2	...	2	15984
Hydrosulphuric acid, }	H.SH	{ 1	7738	1	7738
		{ 2	7802	2	...
Iodic acid, .	H.IO ₃	{ 1	13808	1	13808
		{ 2	14416	2	14000
Hypophosphorus, H.PH ₂ O ₂		{ $\frac{1}{2}$	7695	$\frac{1}{2}$	7637
		{ 1	15160	1	15160
		{ 2	15275	2	15390
<i>Dibasic Acids—</i>					
Sulphuric acid, .	H ₂ .SO ₄	{ $\frac{1}{2}$	7193	$\frac{1}{4}$	7842
		{ 1	14754	$\frac{1}{2}$	15689
		{ 2	31378	1	14754
		{ 4	31368	2	14386

Name of Acid.	Q.	n.	nNaOHAq,QAq).	m.	NaOHAq,mQAq.
<i>Dibasic Acids, con.</i>					
Chromic acid, .	$H_2.CrO_4$	$\left\{ \begin{array}{l} 1 \\ 2 \\ 4 \end{array} \right.$	$\begin{array}{l} 13134 \\ 24720 \\ 25164 \end{array}$	$\begin{array}{l} \frac{1}{4} \\ \frac{1}{2} \\ 1 \end{array}$	$\begin{array}{l} 6291 \\ 12360 \\ 13134 \end{array}$
Sulphurous acid,	$H_2.SO_3$	$\left\{ \begin{array}{l} 1 \\ 2 \\ 4 \end{array} \right.$	$\begin{array}{l} 15870 \\ 28968 \\ 29328 \end{array}$	$\begin{array}{l} \frac{1}{4} \\ \frac{1}{2} \\ 1 \end{array}$	$\begin{array}{l} 7332 \\ 14484 \\ 15870 \end{array}$
Periodic acid, .	$H_2.IH_3O_6$	$\left\{ \begin{array}{l} 1 \\ 2 \\ 2\frac{1}{2} \\ 3 \\ 5 \end{array} \right.$	$\begin{array}{l} 5150 \\ 26590 \\ 28230 \\ 29740 \\ 32040 \end{array}$	$\begin{array}{l} \frac{1}{6} \\ \frac{2}{5} \\ \frac{1}{2} \\ \frac{2}{3} \\ 1 \end{array}$	$\begin{array}{l} 6410 \\ 11290 \\ 13300 \\ 11010 \\ 5150 \end{array}$
Arsenious acid, .	$H_2.As_2O_4$	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \\ 4 \end{array} \right.$	$\begin{array}{l} 7300 \\ 13780 \\ 15070 \\ 15580 \end{array}$	$\begin{array}{l} \frac{1}{4} \\ \frac{1}{3} \\ \frac{1}{2} \\ 1 \end{array}$	$\begin{array}{l} 3895 \\ 5023 \\ 6890 \\ 7300 \end{array}$
Phosphorous acid,	$H_2.PHO_3$	$\left\{ \begin{array}{l} \frac{1}{2} \\ 1 \\ 2 \\ 3 \end{array} \right.$	$\begin{array}{l} 7428 \\ 14832 \\ 28448 \\ 28940 \end{array}$	$\begin{array}{l} \frac{1}{3} \\ \frac{1}{2} \\ 1 \\ 2 \end{array}$	$\begin{array}{l} 9647 \\ 14244 \\ 14832 \\ 14856 \end{array}$
Carbonic acid, .	$H_2.CO_3$	$\left\{ \begin{array}{l} 1 \\ 2 \\ 4 \end{array} \right.$	$\begin{array}{l} 11016 \\ 20184 \\ 20592 \end{array}$	$\begin{array}{l} \frac{1}{4} \\ \frac{1}{2} \\ 1 \end{array}$	$\begin{array}{l} 5148 \\ 10092 \\ 11016 \end{array}$
<i>Tribasic Acid—</i>					
Phosphoric acid,.	$H_3.PO_4$	$\left\{ \begin{array}{l} \frac{1}{2} \\ 1 \\ 2 \\ 3 \\ 6 \end{array} \right.$	$\begin{array}{l} 7329 \\ 14829 \\ 27078 \\ 34029 \\ 35280 \end{array}$	$\begin{array}{l} \frac{1}{6} \\ \frac{1}{3} \\ \frac{1}{2} \\ 1 \\ 2 \end{array}$	$\begin{array}{l} 5880 \\ 11343 \\ 13539 \\ 14829 \\ 14658 \end{array}$
<i>Tetrabasic Acid—</i>					
Pyrophosphoric acid, }	$H_4.P_2O_7$	$\left\{ \begin{array}{l} 1 \\ 2 \\ 4 \\ 6 \end{array} \right.$	$\begin{array}{l} 14376 \\ 28644 \\ 52738 \\ 54480 \end{array}$	$\begin{array}{l} \frac{1}{6} \\ \frac{1}{4} \\ \frac{1}{2} \\ 1 \end{array}$	$\begin{array}{l} 9080 \\ 13184 \\ 14322 \\ 14376 \end{array}$

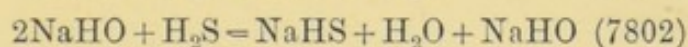
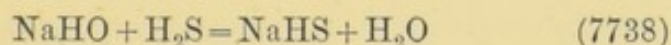
From these results Thomsen concludes :—

1. When a molecule of sodium hydrate in aqueous solution reacts on an acid, the evolution of heat is very nearly proportional to the quantity of the acid until this amounts to 1, $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}$ molecule, according as the acid

is mono-, di-, tri-, or tetra-basic; but if the quantity of acid exceeds that required for the formation of the normal salt, a difference in the behaviour of the various acids becomes apparent, due to their constitution, whereby the evolution of heat may be positive, negative, or *nil*.

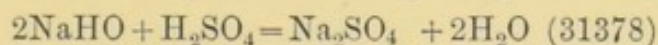
2. If a molecule of an acid in aqueous solution reacts with sodium hydrate, the evolution of heat appears in most cases to be approximately proportional to the quantity of soda, until this amounts to 1, 2, 3, or 4 molecules of sodium hydrate, according as the acid is mono-, di-, tri-, or tetra-basic; but if the quantity of soda be increased beyond this, no important change in the amount of heat evolved takes place in consequence.

Looking at some of the results in the above table, we see clearly the meaning of the two laws above, as well as how we deduce the basicity of the acids. Hydro-sulphuric acid, H_2S , in solution behaves as a monobasic acid, since we get the same evolution of heat from the two reactions—

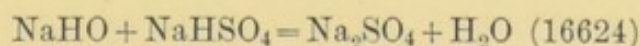


The second molecule of sodium hydrate being apparently without effect.

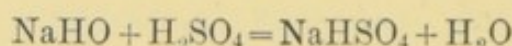
Sulphuric acid, H_2SO_4 , on the other hand, is clearly a dibasic acid—



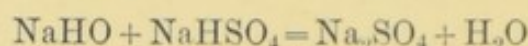
whence



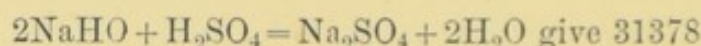
The replacement of the second atom of hydrogen in the sulphuric acid molecule by sodium therefore is attended by the evolution of a larger amount of heat than in the case of the first, in other words, the reaction



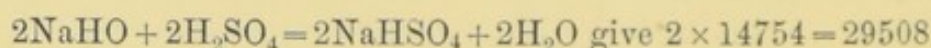
gives less heat than



What then will be the action of more sulphuric acid on the normal sulphate? Obviously an absorption of heat for

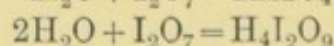
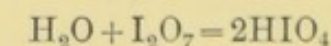


but

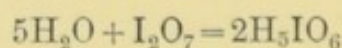


Hence we see the reason of the smaller amount of heat when a larger quantity of sulphuric acid is added than is required for neutralisation.

The behaviour of periodic acid towards bases is much more complicated, but the thermal phenomena seem to point to its being a dibasic acid. Beginning with the anhydride, I_2O_7 , it is obvious we may have many possible acids by combination with varying quantities of water—

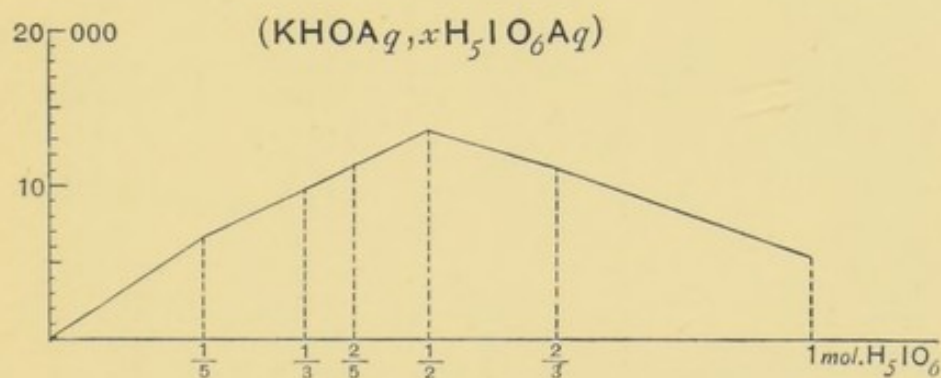
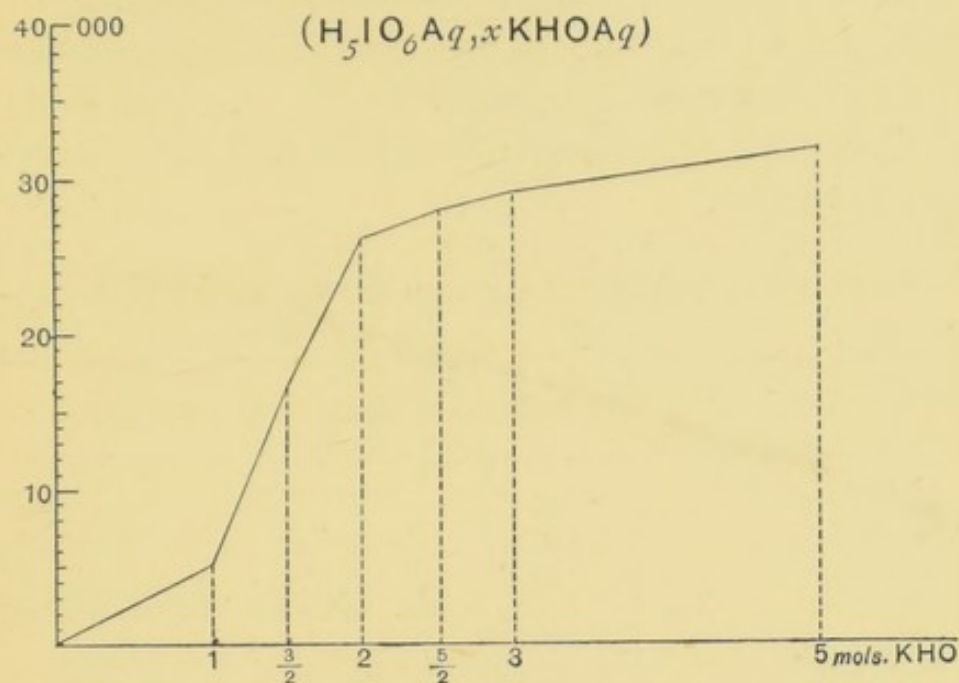


and so on up to



It is very probable that by varying the quantities of the base that we may produce salts of what are really different periodic acids. The very peculiar action of a large excess of acid giving only a small amount of heat is probably due to some such action.

Thomsen graphically represents the reaction thus:—



Taking one acid and the various bases with regard to it, Thomsen finds they may be divided into six groups:—

- A. Alkalies or alkaline earths, including thallious oxide and ammonia.
- B. Bases of the magnesium group.
- C. Sesquioxides.

- D. Oxides of the rarer elements, *i.e.*, lanthanum, cerium, didymium, yttrium, and erbium.
- E. Anhydrous bases, as lead monoxide, oxides of mercury, and silver oxide.
- F. Organic bases, as methylamine, aniline, hydroxylamine.

Some of his results are given in the following tables :—

Q.	(Q, H ₂ SO ₄ Aq).	(Q, 2HClAq).	(Q, 2HNO ₃ Aq).
2KOH Aq . . .	31290	27500	27540
2NaOH Aq . . .	31380	27490	27360
2LiOH Aq . . .	31290	27700	...
2TlOH Aq . . .	31130	27520	27380
BaO ₂ H ₂ Aq . . .	36900*	27780	28260
SrO ₂ H ₂ Aq . . .	30710	27630	...
CaO ₂ H ₂ Aq . . .	31140	27900	...
MgO ₂ H ₂ . . .	31220	27690	27520
MnO ₂ H ₂ . . .	26480	22950	...
CoO ₂ H ₂ . . .	24670	21140	...
FeO ₂ H ₂ . . .	24920	21390	...
ZnO ₂ H ₂ . . .	23410	19880	19830
CuO ₂ H ₂ . . .	18440	14910	14890
CuO . . .	18800	15270	15250
PbO . . .	23380*	15390	17770
HgO	18920	6210
Hg ₂ O	30070*	5790
Ag ₂ O . . .	14490	42380*	10880
2NH ₃ . . .	28150	24540	24640
2N(CH ₃) ₄ OH Aq .	31030	27490	...
2NH ₂ (CH ₃)Aq	26230	...
2N(CH ₃) ₃ Aq . .	21080	17480	...
2NH ₂ (OH)Aq . .	21580	18520	...
2NH ₂ (C ₆ H ₅)Aq .	18480

* One notices the large values obtained when the result is an insoluble salt, as BaSO₄, PbSO₄, Hg₂Cl₂, AgCl. We have the heat due to the physical change of state along with that due to the chemical action.

Q.	(Q, 3H ₂ SO ₄ Aq).	(Q, 6HClAq).
La ₂ O ₃ .xH ₂ O . .	3 × 27470	3 × 25020
Ce ₂ O ₃ .xH ₂ O . .	3 × 26030	3 × 24160
Al ₂ O ₃ .xH ₂ O . .	3 × 20990	3 × 18640
Cr ₂ O ₃ .xH ₂ O . .	3 × 16440	3 × 13730
Fe ₂ O ₃ .xH ₂ O . .	3 × 11280	3 × 11150

The evolution of heat on neutralisation for the magnesia group was determined from the heat evolved on decomposition of the sulphates in solution by baryta-water. The evolution of heat thus obtained was due to the difference between the heats of neutralisation of baryta and the hydrate in question—

$$(\text{MgH}_2\text{O}_2\text{Aq}, \text{H}_2\text{SO}_4\text{Aq}) = (\text{BaH}_2\text{O}_2\text{Aq}, \text{H}_2\text{SO}_4\text{Aq}) - (\text{MgSO}_4\text{Aq}, \text{BaH}_2\text{O}_2\text{Aq})$$

$$x = 36896 - 5840$$

$$x = 31056$$

also

$$(\text{MgH}_2\text{O}_2\text{Aq}, \text{H}_2\text{SO}_4\text{Aq}) = (2\text{KOH}\text{Aq}, \text{H}_2\text{SO}_4\text{Aq}) - (\text{MgSO}_4\text{Aq}, 2\text{KOH}\text{Aq})$$

$$x = 31288 - (-88)$$

$$x = 31288 + 88 = 31376$$

$$\text{Mean value} = \left(\frac{31056 + 31376}{2} \right) = 31216$$

Similarly for the sesquioxide group—

$$(\text{Fe}_2\text{O}_6\text{H}_6\text{Aq}, 6\text{HClAq}) = 6(\text{NaOH}\text{Aq}, \text{HClAq}) - (\text{Fe}_2\text{Cl}_6\text{Aq}, 6\text{NaOH}\text{Aq})$$

$$x = 6(13744) - 49008$$

$$x = 82464 - 49008$$

$$x = 33456 = 3 \times 11152$$

The average difference of eight acids is 507; but with sulphuric acid we have 5518, indicating, what is pointed out below, that much heat is produced by the formation of a solid (barium sulphate).

Comparing the heat evolved by neutralising various acids with two bases, soda and baryta, he got—

Acid.		2NaHO.	BaH ₂ O ₂ .	Difference.
Sulphuric,	H ₂ SO ₄ .	31378	36896	5518
Chloric,	2HClO ₃ .	27518	28056	538
Hydrochloric,	2HCl .	27488	27784	296
Nitric,	2HNO ₃ .	27364	28264	900
Acetic,	2HC ₂ H ₃ O ₂	26790	26904	114
Hydrosulphuric,	2HSH .	15476	15748	272

The law of thermo-neutrality of Hess, which stated that, when we have the double decomposition of neutral salts in solution, heat is neither evolved nor absorbed, is not strictly true. From the tables given above, it is apparent that the differences between the amounts of heat given out on neutralisation by any two bases and a series of acids are practically the same, and similarly for any two acids with a series of bases. Hence, on double decomposition of two salts, we have at most small thermal changes if all the products remain in solution, and the acids are of a normal type.

One very interesting problem, but a very hard one to solve satisfactorily, and which we must leave till the next chapter, is—Suppose we take one equivalent of potash, and add one equivalent of nitric acid and one equivalent of sulphuric acid, how is the potash shared by the two acids? Does the sulphuric acid take it all and completely prevent the nitric acid from having any, or not?

CHAPTER X.

CHEMICAL CHANGE.

CHEMISTRY has to deal with the changes in the structure of the individual molecules of which a mass of any kind may be made up, whereas physics has to deal chiefly with the molecules in a state of aggregation. The former studies the internal arrangement and relations of the parts of the molecule to one another, while the latter has to take note of the relations of the whole molecules to one another.

A chemical change then is one which affects the arrangement and the number of the atoms in a molecule. A physical change affects the state of aggregation of the molecules and their action as a mass. Water in the form of steam, water, and ice, has in each the same relative composition of eight parts by weight of oxygen to one part of hydrogen. As far as we can discover, each molecule in any one of the three forms is made up in this way. Similarly, when we heat red mercuric oxide carefully, so as to lose neither mercury nor oxygen, it becomes black, and when allowed to cool it regains its original red colour; when black, just as when red, as far as we know, its composition is two hundred parts of mercury united to sixteen parts of

oxygen. Its action on light varies, but each molecule seems to remain the same. If we heat it further, however, we easily separate the mercury atoms from the oxygen atoms, and thus have a chemical change.

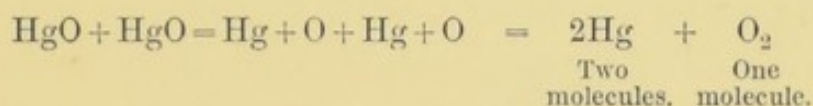
Chemical changes may be referred to a few typical classes, of which the chief are :—

1. *Analysis*, or the formation of two or more simpler molecules from a complex one.
2. *Synthesis*, or the formation of more complex molecules from simpler ones.
3. *Substitution*, or the formation of a new molecule by the withdrawal of an atom or group of atoms (a radical), and its simultaneous replacement by an equivalent atom or radical.
4. *Isomeric change*, or the formation of a distinctly new molecule or molecules, having the same relative composition as those from which they were formed.

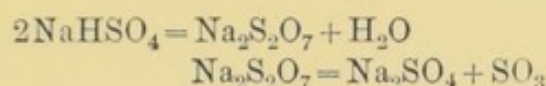
With regard to the first, in its simplest form, which we may call *true analysis*, or the separation of a molecule into its constituent atoms, we have many examples as the first stage of further chemical changes, but very few in which the result of this analysis remains as the final stage of the change, unless at very high temperatures, since the atoms, even when alike, tend to form themselves into molecules when the temperature is low.

For the commoner cases of analysis, which we may term *proximate analysis*, we have very numerous

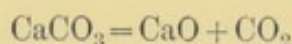
examples, as in the substance above referred to, red mercuric oxide, which, when heated, breaks into mercury and oxygen atoms, as in a true analysis ; but this is not the final stage, for the oxygen atoms unite in pairs, while the mercury atoms remain free —



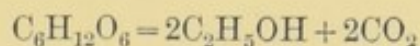
Sodium hydrogen sulphate, when heated, gives sodium pyrosulphate and water, and the sodium pyrosulphate gives sodium sulphate and sulphur trioxide—



Calcium carbonate (limestone), when heated, breaks up into calcium oxide (quicklime) and carbon dioxide—

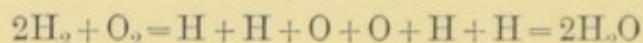


Glucose or grape-sugar, when its solution is fermented, breaks up into alcohol and carbon dioxide—

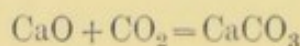


In the same way we may regard synthesis as of two kinds, *true synthesis* being characterised by the formation of a molecule from free atoms ; this can happen only at temperatures high enough for the existence of free atoms, and is usually preceded by a true analysis. In the formation of steam from a mixture of oxygen and hydrogen, we apply a light and decompose a few of the molecules of each gas into their component atoms ; and these, instead of reforming the original molecules of the element, form stabler ones of the compound with

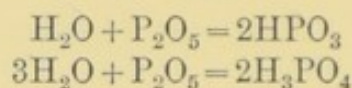
the evolution of much heat, which decomposes fresh molecules in turn, just as the light applied did, till all have combined, as



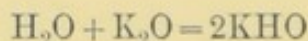
Proximate synthesis is the formation of a new molecule from two or more simpler ones, as calcium oxide unites with carbon dioxide to form calcium carbonate—



Water and phosphorus pentoxide unite to form metaphosphoric acid, HPO_3 , or ortho-phosphoric acid, H_3PO_4 —

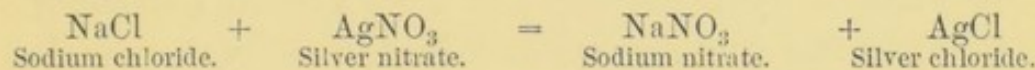
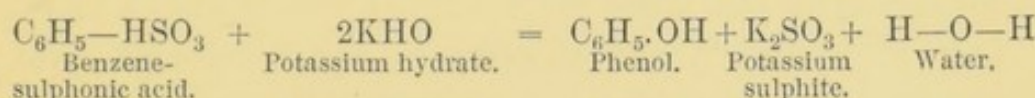
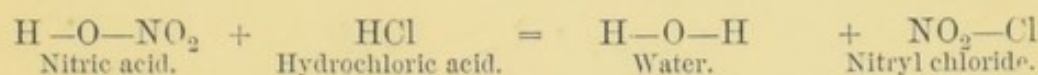


Water and potassium oxide unite to form potassium hydrate—

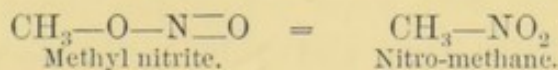
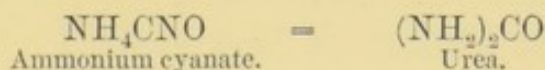


Substitution is a very common method of forming new molecules, and in its widest sense may be regarded as almost the same as double decomposition. Gerhardt regarded all chemical changes as being of the nature of double decomposition; and although we hardly go so far as that, there is no doubt that the majority of reactions may be thus regarded. What we mean by double decomposition is, that if we regard two molecules as being each composed of two parts, when they react on one another the bodies formed will also consist of the same parts, but arranged in another way. If we have a molecule AB composed of A and B , and ab composed of a and b , then when AB acts on ab we have Ab and $a\text{B}$ produced by the reaction.

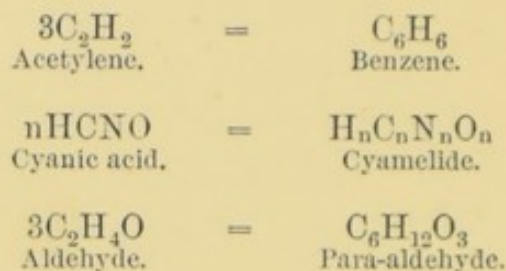
The following examples will make this plainer :—



Isomeric change occurs very frequently with bodies of which the molecule is a complex one, and of which the atoms in the molecule, being numerous, can rearrange themselves in more or less stable forms. The most interesting case historically is the change of ammonium cyanate into urea :—



Polymerisation occurs when the molecular weight of the new body is a multiple of that of the original substance, the percentage composition of both being the same, as



Why do these reactions take place at all, and what is the cause of the chemical changes? Why does a mixture of hydrogen and chlorine in equal volumes give rise to an equal volume of hydrochloric acid, whilst a mixture of hydrogen and iodine vapour does not tend to produce hydriodic acid; or if we prepare a quantity of hydriodic acid gas and mix it with chlorine, why do we get hydrochloric acid gas and free iodine? We usually say that the hydrogen has a greater affinity for chlorine than for iodine, and that the combination of hydrogen with chlorine gives out more heat than that of hydrogen with iodine. As the tendency in by far the larger number of chemical reactions is to evolve heat, and so get into a stabler condition by a degradation of energy, it is sometimes stated that we can measure the affinity by the amount of heat evolved. That this is not so, however, we can easily prove.

Chemical affinity has been compared to universal gravitation, but with these differences—that it only acts at very small distances and is distinctly elective, that is to say, it acts readily between some bodies and not with others. The result of the attraction is a combination of

the two substances apparently by the impact of the atoms with an evolution of heat, just as a body falling to the earth by the mutual attraction between it and the earth gives rise to heat by percussion on their collision.

As to its real nature we are at present quite ignorant, but much that is interesting and important is known.

Why do we say that chlorine has a great affinity or attraction for hydrogen when it can only take one atom for each atom of itself, whereas we say nitrogen has but little affinity for hydrogen, yet each atom requires three atoms of hydrogen to satisfy it? In the same way we say that potash is a stronger base than soda, and this again than ammonia. It takes 56 parts of potassium hydrate to neutralise 63 parts of nitric acid, but only requires 40 parts of sodium hydrate, and, still less, only 17 parts of ammonia. One part of potassium hydrate only neutralises $\frac{63}{56} = 1\frac{1}{8}$ part of nitric acid, but 1 part of sodium hydrate neutralises $\frac{63}{40} = 1\frac{3}{8}$ of nitric acid, while 1 part of ammonia neutralises $\frac{63}{17} = 3\frac{1}{17}$ parts of nitric acid. Ought we not, then, to say that ammonia is the strongest base of the three?

In the same way, to take one base, soda, and various acids, to neutralise 40 parts of sodium hydrate, 49 parts of sulphuric acid, 63 parts of nitric acid, or $36\frac{1}{2}$ parts of hydrochloric acid are required. Is hydrochloric acid the strongest and nitric acid the weakest of these three acids?

Before investigating this problem further, we will take some other and simpler cases, illustrating to some extent at least the elective action of affinity, such as the replacement of one element by another. To some such

cases we have already referred when considering the classification of the elements.

Metallic silver is readily dissolved by nitric acid, and gives a solution of silver nitrate, which, on evaporation, may be obtained in the solid form and quite free from acid reaction. On dissolving some of this solid in water, and introducing a piece of metallic copper, the liquid acquires a blue colour due to the solution of copper nitrate, while the copper strip becomes covered by a lustrous grey powder of metallic silver, which weighs exactly the same as the silver from which the silver nitrate was made; the copper, however, has lost considerably in weight. For every 108 parts of silver deposited we have $31\frac{3}{4}$ of copper dissolved, but this may in turn be deposited by placing a piece of iron or zinc into the blue solution till its colour disappears, when our $31\frac{3}{4}$ parts of copper will be recovered as a brown powder, but at the expense of 28 parts of iron or $32\frac{1}{2}$ of zinc. In these experiments we have proved that the affinity of zinc for the nitric acid radical is greater than that of copper for it, but this in turn is greater than that of silver. At each replacement we have also a distinct and definite evolution of heat. Similarly, if we take solution of potassium iodide, and add to it bromine carefully, we can replace the whole of the iodine by bromine, and obtain a solution of potassium bromide and free iodine; by passing now chlorine gas into the potassium bromide solution, we in turn obtain a solution of potassium chloride and free bromine. With these changes also we have a simultaneous evolution of heat, perfectly definite in amount.

Under other circumstances iodine may turn out chlo-

rine from its compounds, and notably those with more electro-negative elements. On boiling a solution of potassium chlorate acidified with nitric acid (really a solution containing free chloric acid), we have chlorine steadily evolved, and iodic acid and potassium iodate formed. Here, then, we have iodine indicating that its affinity for oxygen is greater than that of chlorine, although its affinity for hydrogen is much less.

Many external circumstances, however, as has been pointed out already, modify the changes which would be produced under the influence of affinity alone, notably the temperature and mass as well as solubility, volatility, and such like properties of the bodies reacting or being produced. The mere measurement of heat evolved in a reaction does not give a measure of the affinity or *intensity* of the chemical forces, but only of the work done by them. How, then, can we obtain any measurement of affinity?

When solutions of two salts, such as potassium chloride and sodium nitrate, are mixed, we have undoubtedly a reaction resulting in the formation of four salts, each base sharing both acids. In this way it is possible to cause an exchange, more or less complete, of the acid from one base to the other when we have any great difference of solubility. On mixing solutions of the two salts mentioned, we have the four possible salts, potassium nitrate, potassium chloride, sodium chloride, sodium nitrate formed. After a time we have equilibrium established, and this state of equilibrium depends on the proportions in which the original salts are mixed. If we remove one of these salts in any way (by precipitation, &c.) it tends to reform again, and may again be removed. When we

evaporate such a solution down, sodium chloride is the first to separate out ; as it is formed and separated more and more, we have equivalent quantities of potassium nitrate formed, and on cooling it will in turn crystallise out almost pure. The cold solution may again be boiled down when the same changes are repeated.

We have many other cases in which it is quite apparent that we have a chemical change going on when two solutions are mixed, even although we may have no precipitation.

The majority of our ordinary qualitative and quantitative tests depend on double decomposition of this nature. If we mix solutions of sodium sulphate and barium chloride, we have the possible formation of sodium chloride and barium sulphate along with the two original salts. The barium sulphate, however, is so insoluble that it separates at once, more and more is formed till no more is possible, and this happens when either the whole of the barium or of the sulphuric acid is precipitated. It takes a long time for such a reaction to become quite complete, if it ever does so, even from a practical point of view.

When we have all the salts remaining in solution we can still prove that we have a change, and the influence of the one salt on the other in the formation of the two other salts possible have been determined in several cases by making use of such effects as change of colour, refractive index, volume, &c., on mixture.

When ferric nitrate, $\text{Fe}_2(\text{NO}_3)_6$, and potassium thiocyanate, KCNS, are mixed in solution, we have the well-known blood-red solution formed, due to the presence of ferric thiocyanate. If we mix the salts in equivalent

proportions, and compare the colour thus produced with the colour of the amount of pure ferric thiocyanate which could be produced, we can determine what fraction of the equivalent has changed. On adding more and more potassium thiocyanate we get a stronger and stronger colour; yet we never have the whole of the iron changed into thiocyanate, even when the solution contains nearly four hundred times the amount of thiocyanate required.

Gladstone gave the following measurements for one equivalent of ferric nitrate:—

Molecules of Potassium Thiocyanate.	Red Salt produced.	Molecules of Potassium Thiocyanate.	Red Salt produced.
3	88	63	356
6	127	99	419
9.6	156	135	487
12.6	176	189	508
19.2	213	243	539
28.2	266	297	560
46.2	318	375	587

Taking the first at about 13 per cent., with 375 molecules we have only got about 87 per cent. of the iron into the condition of red thiocyanate; the other 13 per cent. of the iron still remaining as nitrate.

In a similar way, on adding hydrochloric acid to a solution of copper sulphate, we have the blue colour change to green or greenish yellow, according to the proportion of hydrochloric acid, and hence copper chloride formed. We have here the base, copper oxide dividing itself between the hydrochloric and the sulphuric acid present, and many actions of this kind have been carefully studied.

If chemical affinity be a true force, we can find under given circumstances what are the essential conditions for equilibrium. This is what may be called the *statical* method of measuring it. We may also, however, determine in many cases the rate of chemical change, and thus measure the intensity of the forces at work by a *kinetic* method. It is a force, as it can cause motion of the molecules, and be converted definitely into other forms of energy.

Thomsen showed that although, when we neutralise soda with hydrofluoric acid, a far larger evolution of heat is produced than with hydrochloric acid, yet when hydrochloric acid is added to sodium fluoride, sodium chloride and hydrofluoric acid were formed with a large *absorption* of heat. Here, then, is a case of a chemical change taking place, and with a large absorption of heat, and proving clearly that we cannot measure the affinity between two substances by the amount of heat evolved when they react. The numbers relating to the experiment are (using the notation employed in the last chapter) :—

	Difference.
(NaOHAq, HFAq) = +16272	} 2532
(NaOHAq, HClAq) = +13740	
(NaFAq, HClAq) = - 2362	

from which it follows that about 93 per cent. of the sodium fluoride is decomposed.

The *avidity*, as Thomsen terms it, of hydrofluoric acid for soda is therefore very feeble.

In a similar way, by acting on sodium sulphate with an equivalent quantity of nitric acid, he showed that nitric acid, quite contrary to our ordinary notions, is

really much more powerful than sulphuric acid, and that two-thirds of the soda combine with the nitric acid, leaving only one-third for the sulphuric acid. The partition of the base is quite the same whether sodium sulphate and nitric acid, or sodium nitrate and sulphuric acid, are the original substances.

Thomsen gives the following results of his experiments on the affinity (avidity) of acids for bases :—

Acid.	Formula.	Affinity.	Heat of Neutralisation.
1 molecule of nitric, . . .	HNO_3	1.00	13680
1 " " hydrochloric, .	HCl	1.00	13740
1 " " hydrobromic, .	HBr	.89	13750
1 " " hydriodic, . .	HI	.79	13680
$\frac{1}{2}$ " " sulphuric, . .	$\frac{\text{H}_2\text{SO}_4}{2}$.49	15690
1 " " trichloroacetic, .	$\text{CCl}_3.\text{CO}_2\text{H}$.36	13920
1 " " orthophosphoric,	H_3PO_4	.25	14830
$\frac{1}{2}$ " " oxalic, . . .	$\frac{\text{H}_2\text{C}_2\text{O}_4}{2}$.24	14140
1 " " monochloroacetic,	$\text{CH}_2\text{Cl}.\text{CO}_2\text{H}$.09	14280
1 " " hydrofluoric, .	HF	.05	16270
1 " " acetic, . . .	$\text{CH}_3\text{CO}_2\text{H}$.03	13400
$\frac{1}{2}$ " " boracic, . . .	$\frac{\text{B}_2\text{O}_3}{2}$ or HBO_2	.01	10005

Ostwald has utilised in a similar way the volume relations of acids, bases, and salts in dilute solution, and has deduced almost exactly the same values for the affinities of the various acids.

The solutions he uses contain, as a rule, one molecular weight in grams in one kilogram of solution. The volume of such a solution would be for potassium hydrate 950.668 c.c., for nitric acid 966.623 c.c. On

mixing one kilogram of each we of course obtain two kilograms (or 2000 grams), and the volume is 1937·338 c.c. ; but $950\cdot668 + 966\cdot623$ are equal to 1917·291, which shows that on neutralisation we have an expansion of 20·047 c.c. on neutralisation. By employing other acids we get corresponding results, and then by acting on solutions of salts by acids changes of volume occur, from which the extent of the chemical change may be deduced in the same way as Thomsen employed the heat phenomena.

He gives the following values for several acids :—

Acid.	Formula.	Affinity.
Nitric,	HNO_3	1·00
Hydrochloric,	HCl	·98
Trichloroacetic, . . .	$\text{CCl}_3\cdot\text{CO}_2\text{H}$	·80
Monochloroacetic, . . .	$\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$	·07
Acetic,	$\text{CH}_3\cdot\text{CO}_2\text{H}$	·0123
Tartaric,	$\text{C}_2\text{H}_2(\text{OH})_2(\text{COOH})_2$	·052

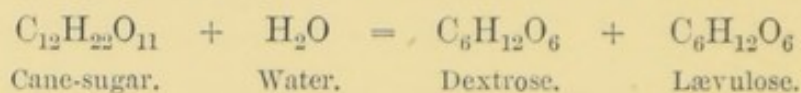
To determine whether the base had any effect on the relative affinities, many experiments were made, the results of which are given in the following table, which in column 1 gives the ratio in which the bases are divided between nitric and sulphuric acid ; 2, the same for hydrochloric and sulphuric acids ; and 3, the results in column 2 divided by those in column 1, thus giving the affinity of hydrochloric acid in terms of that of nitric acid, from which it is very evident that the relative

affinities of these two acids are independent of the base :—

		Nitric. Sulphuric.	Hydrochloric. Sulphuric.	Hydrochloric. Nitric.
Potash,	KHO .	$\frac{.667}{.333} = 2.00$	$\frac{.659}{.341} = 1.94$	$\frac{1.94}{2.00} = .97$
Soda,	NaHO .	$\frac{.667}{.333} = 2.00$	$\frac{.657}{.343} = 1.92$	$\frac{1.92}{2.00} = .96$
Ammonia,	NH ₃ .	$\frac{.652}{.348} = 1.88$	$\frac{.644}{.356} = 1.81$	$\frac{1.81}{1.88} = .96$
Magnesia,	MgO .	$\frac{.638}{.362} = 1.76$	$\frac{.635}{.365} = 1.74$	$\frac{1.74}{1.76} = .99$
Zinc oxide,	ZnO .	$\frac{.617}{.383} = 1.61$	$\frac{.605}{.395} = 1.53$	$\frac{1.53}{1.61} = .95$
Copper oxide,	CuO .	$\frac{.599}{.401} = 1.49$	$\frac{.584}{.416} = 1.40$	$\frac{1.40}{1.49} = .97$

It is by no means easy to determine accurately the rate of chemical change in ordinary reactions, as not only are the quantities of the reacting substances constantly changing, but other substances are being produced which modify the principal change by their presence. One or two examples, however, may be looked at with advantage. One of the simplest is the "inversion" of cane-sugar, which is dextro-rotatory, but on hydration it changes into two new bodies—dextrose and lævulose, of which the lævulose is more powerfully lævo- than the dextrose is dextro-rotatory; hence, when the change is complete our dextro-rotatory cane-sugar becomes a lævo-rotatory mixture of dextrose and lævulose. The change can be noted while it progresses, and no by-products seem to be formed. It, however, requires

the presence of an acid, and we may compare the power of the various acids to induce the change, which may be simply represented thus—



In the same way many ethers, which are readily decomposed by water when heated with it, react very slowly when cold, but much more rapidly when a small quantity of an acid is added to them. Ostwald used methyl acetate, which only decomposes into methyl alcohol and acetic acid to the extent of 1 per cent. in two or three days with pure water; but if a small quantity of an acid be added, it may be completely resolved into alcohol and acid in one day. The change is readily measured by determining the increasing amount of acid at given intervals of time.

Another change, which has been investigated in a similar way, but which is not so free from secondary reactions, is the breaking up of acetamide into ammonia and acetic acid in presence of water and a strong acid, the mainspring of the action being the tendency of the acid and ammonia to combine.



As the change proceeds, it is evident we have larger and larger quantities of acetic acid produced, whilst more and more acetamide and strong acid disappears. Some of the numbers obtained by Ostwald by various methods are tabulated below for comparison. Those in column I. are derived from experiments on acetamide;

in column II., from "inversion" of cane-sugar; in column III., from methyl acetate.

Acid.	I.	II.	III.
Hydrochloric, .	1·000	1·000	1·000
Nitric, .	·955	1·000	·915
Hydrobromic, .	·976	1·114	·983
Trichloracetic, .	·670	·754	·682
Monochloracetic, .	·0295	·0484	·043
Acetic, .	·000747	·0040	·00345
Sulphuric, .	·547	·536	·547
Oxalic, .	·169	·1857	·1746
Phosphoric, .	·0449	·0621	...

From these results, arrived at by methods so very different in character, we see clearly the order at least, if not the very accurate value, of the affinity of various acids. For further information on this subject the original papers published by Ostwald and others should be consulted.

Many chemical changes seem to be induced by small quantities of foreign bodies, as in those decompositions above referred to, methyl acetate and water becoming methyl alcohol and acetic acid, a change taking place with extreme slowness, even when large amounts of water are present, but very readily when a strong acid, such as hydrochloric acid, is present. It might be supposed that the hydrochloric acid combined with the alcohol to form methyl chloride. If this were so, then the hydrochloric acid which so combined would be unaffected by a solution of silver nitrate. On testing, however, all the chlorine reacts with the silver nitrate throughout the whole reaction. In the same way, with

the inversion of cane-sugar the attraction seems to be between the hydroxyl groups in the sugar and the radical of the acid, but the full amount of acid seems to be in the free state the whole time.

A very familiar example is the action of manganese dioxide in bringing about the rapid evolution of oxygen from potassium chlorate at a much lower temperature than that required for the pure chlorate. Here we seem to have a tendency to form manganese trioxide from the dioxide and oxygen; and as this is unstable at the high temperature, it cannot exist even if ever formed. If, however, a quantity of the hydrate be mixed with the chlorate, we get the manganate formed in large quantity, and in which we have the manganese trioxide forming a compound with the potassium oxide, stable at the high temperature.

In quite a similar way hydrogen peroxide may be resolved into water and oxygen, which comes off readily with effervescence when small quantities of finely-divided platinum, silver, or manganese dioxide are added. Actions of this kind, in which definite changes were brought about on large quantities of materials by relatively very small quantities of another substance, which itself appeared to remain throughout the reaction perfectly unchanged in properties and amount, were said to be *catalytic*. In a great many reactions formerly so-called investigation has clearly shown the part which is played by the catalytic agent; as, for example, in the use of the nitrogen peroxide in the manufacture of sulphuric acid, and of sulphuric acid itself in the continuous etherification process.

A change at first sight of the same kind, which has been

known and made use of in all countries and in all ages, is that of the saccharine juices of plants into alcoholic and intoxicating beverages. Here the sugar in the liquid changes into ethyl alcohol and carbon dioxide, but an ordinary solution of glucose, especially after having been boiled, never gives off carbon dioxide or becomes alcoholic when kept in a carefully closed vessel. If, however, a small quantity of the yeast plant be introduced, the change above indicated begins and proceeds at a rapid rate if suitable food materials for the plant be also present, the plant growing rapidly meanwhile. In this, then, it differs somewhat from a true catalytic reaction, but as such it was regarded to be till 1838. A change of this kind, depending in some way or other on a living organism for its progress, is termed *fermentation*. The name, literally meaning a boiling-up, was derived from the frothing taking place in the ordinary alcoholic fermentation.

The part played in such chemical changes by ordinary air has been thus traced. It was found that a solution of boiled grape-juice could be preserved indefinitely in a vacuum, but on admitting air the chemical change began; but if the air before admission were caused to pass through a red-hot tube, the grape juice might be preserved indefinitely at the ordinary pressure and in presence of such air. Clearly, it is not the air but something in it, and which is destroyed by a red heat, that is the primary cause of the change. Another clear proof that it was something in the air of the nature of particles was given by filtering the air through cotton-wool, when such air was found to be like that passed through the red-hot tube. It was further

proved that the liquid filtered from ordinary yeast was incapable of inducing fermentation, but that the semi-solid mass remaining on the filter possessed that power in a high degree. Many other chemical changes take place in organic liquids only when ordinary air is allowed more or less free access to them, but which may be preserved indefinitely in pure air if no contamination has been allowed to take place. Very common cases are milk turning sour and meat or meat extracts putrefying. In each of these cases Pasteur clearly showed that there was a special organism, and that the particular fermentation was closely connected with the growth and the development of that organism. The question is, then, are these various organisms the cause or are they the result of the fermentation, or are they merely accidental accompaniments of the process? There is but little doubt that somehow or other they are the cause; for, as we have seen, they grow in the fermenting liquid, and it is only while they are growing that the process goes on, and that if they be killed the process stops entirely. An agent which kills the organisms and thus stops fermentation is termed an *antiseptic*. The study of fermentation has the very greatest interest, and is of the greatest importance with regard to the preservation of animal food and to medical science, since there is little doubt that many diseases are due to, or at least are very closely connected with, fermentations taking place in the animal body, the particular disease depending on the particular organism then residing and growing in the body. This theory that diseases are due to such organisms or "germs" affords a very simple explanation of infectious diseases. The specific germs have been

definitely identified in the cases of several fevers, although not for all.

There is still one question to be decided, and that is how these organisms act? Do they feed on the original substance, and are the final products of the nature of excretions? or do they, while growing, produce a substance which acts like the catalytic agents above referred to? This latter view is more probable, since the total volume of the organisms is so very small compared with the amount of matter which undergoes transformation, and with the rapidity at which it progresses. According to Pasteur, it is probable that not more than 1 per cent. of the sugar which is fermented is used by the yeast itself. In the manufacture of alcoholic liquids from barley, the first change of the nature of a fermentation is that of the starch in the grain into the sugar which is in the malt. This change is brought about by the presence of an unorganised ferment known as diastase. It is not a living substance, but is the direct product of a living organism. It is, then, highly probable that in fermentations caused by living organisms, substances analogous to diastase are produced, and that these soluble substances are the true ferments or catalytic agents. Some of these have been prepared by extraction with water from the cells containing them, and then precipitating them from their solution by alcohol or some other reagent. The ptyalin in the saliva and the pepsin in the gastric juice belong to this class.

Very many of the actions produced by ferments are of a simple character, at least in their final results, such as separation or addition of the elements of water or of oxygen.

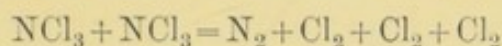
Another interesting class of reactions, which are of very great importance, comprises those brought about by more or less decided mechanical contacts, such as the decomposition of nitrogen iodide into its elements, which may be begun by the touch of a feather, the work expended on the contact having no relation whatever to the work which may be done. Other substances, such as glyceryl trinitrate (nitro-glycerine) require a much stronger blow to cause their decomposition, such as a powerful blow on an anvil with a heavy hammer, but which will quietly burn away when kindled with a flame. Bodies of this kind, and which are termed explosive, form by their decomposition simpler substances generally gaseous in nature, and with the evolution of much heat. The production of an enormous volume of gas with great rapidity from a relatively minute volume of material, is an essential quality in explosives for practical purposes.

Explosive compounds are either formed with a large absorption of heat, and hence give it back on decomposition, or are unstable, because by a rearrangement of their atoms into simpler molecules a large amount of heat may be generated.

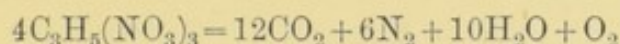
Of the former class nitrogen iodide and chloride, chlorine peroxide, carbon disulphide, and hydriodic acid gas may be taken as typical examples. Of the second, ethyl nitrate, tri-nitrophenol (picric acid), the fulminates, glyceryl trinitrate, and cellulose trinitrate are good examples.

In the simpler case, when we have a compound breaking up into its elements with an evolution of heat, as nitrogen chloride, we have almost a proof of the combination of the atoms of elements into molecules, and that the state

of molecules of elementary nitrogen and chlorine is more stable than that of molecules containing both, hence



that is, the attraction of the nitrogen for the nitrogen and of the chlorine for chlorine is greater than that of nitrogen for chlorine. In the second case, we have generally organic radicals united to radicals containing more or less oxygen. The oxygen in glyceryl trinitrate is rather more than sufficient to burn up completely all the carbon and hydrogen in the molecule into water and carbon dioxide—



If the oxygen is in too great an excess, it interferes seriously with the explosiveness, as in tetra-nitromethane $\text{C}(\text{NO}_2)_4$, which is not explosive, but nitroform $\text{CH}(\text{NO}_2)_3$, is. The fulminates are remarkably explosive, mercuric fulminate $\text{NO}_2\text{HgC.CN}$, being the substance employed in percussion caps, &c., for starting the explosion in other explosive materials.

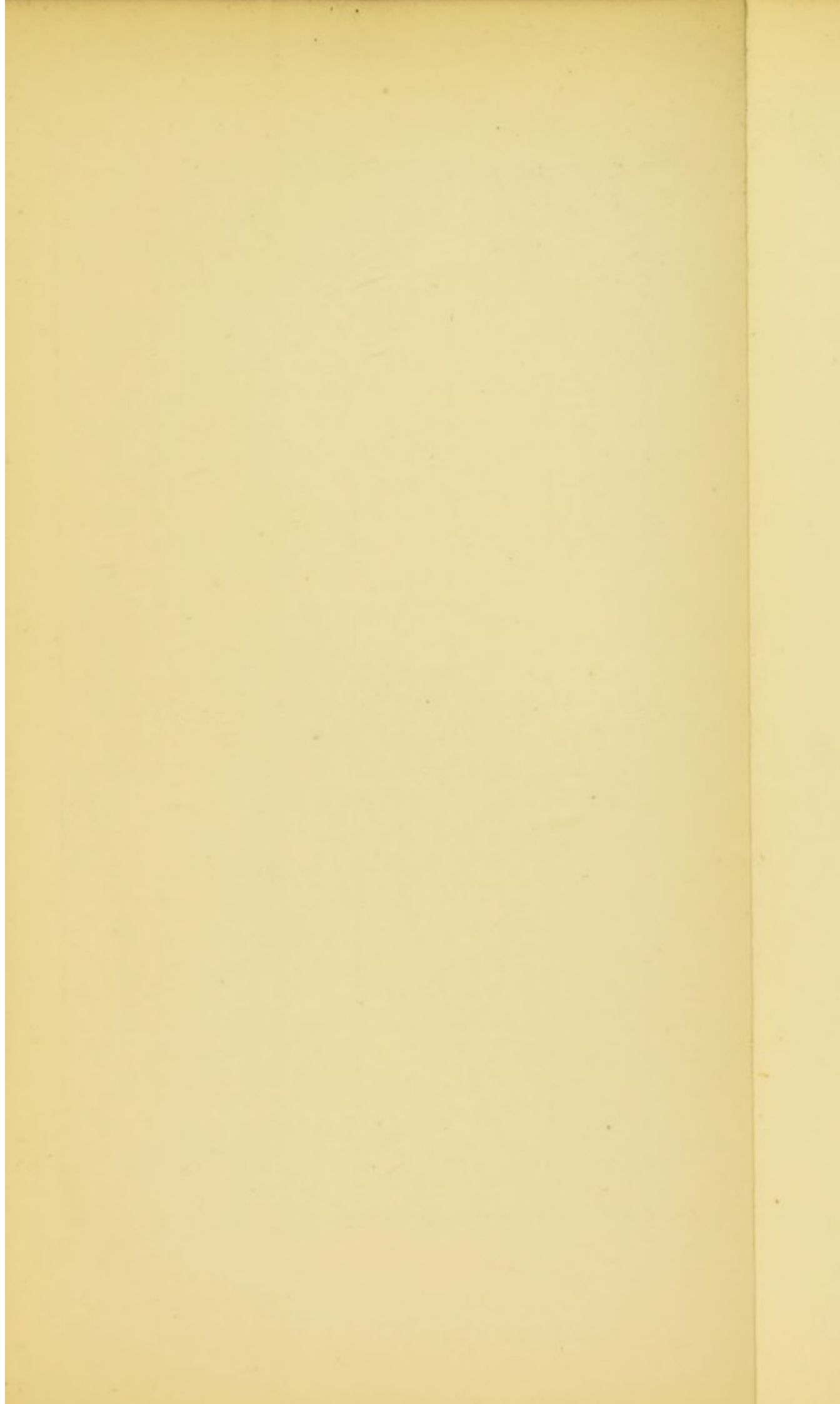
The much greater violence exerted by purely chemical explosives such as nitro-glycerin, compared with such mechanical mixtures as gunpowder, is due to the enormously greater velocity of the explosion in what we may call molecular explosives, where we have all the necessary oxygen within the molecule instead of being at the much greater distance necessarily involved by its being in a particle merely adjoining and at a measurable distance. The more thorough the mixture the more rapid will the combustion be, hence the rapid or explosive combination in the case of a mixture of gases such as hydrogen and oxygen.

CHAPTER XI.

SOLUTION AND ELECTROLYSIS.

WHEN a solid, such as common salt, is added to water it disappears from view, taking the liquid form, generally with an absorption of heat, which is often very considerable, and leads to the employment of such substances as ammonium nitrate for freezing mixtures. If we keep gradually adding the salt in small quantities, we find a time comes when no more salt will be taken up or dissolved by the liquid *at that temperature*, the liquid is then said to be *saturated* with the solid. As a general rule, as previously pointed out (page 18), if the temperature be raised more solid will be dissolved, and this on cooling will be deposited in the crystalline form, thus enabling us to purify many substances when contaminated by the presence of small quantities of impurities. The process may be repeated as often as is necessary, and is termed *recrystallisation*.

The definiteness of the amount for each temperature, and its increase by rise of temperature in by far the larger number of cases, suggests some similarity to the phenomena of dissociation. If we compare, however, the rates of increase of solubility for different substances by increase of temperature, we find they vary in a way quite unlike the rates of dissociation of different sub-



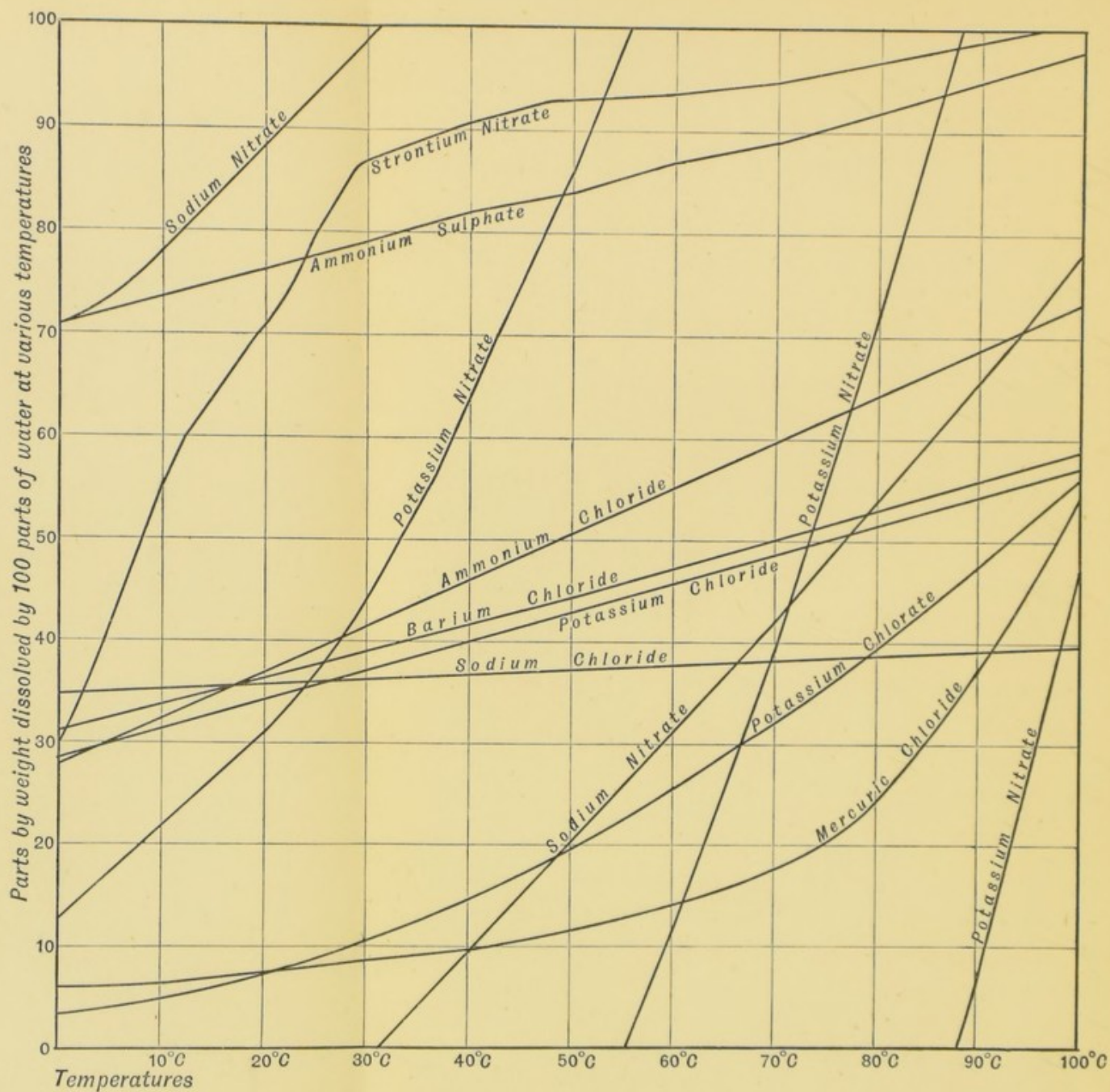


Diagram of Solubilities, after Gay Lussac (page 249).

stances. Common salt is very little more soluble in boiling water than in water at the ordinary temperature ; but nitre is very much more soluble in hot than in cold water, 100 parts of water at 0°C . dissolving 13 parts, water at 50°C . 86 parts, and water at 100°C . 247 parts. For common salt the corresponding amounts are respectively 35.5, 37, and 39.6 parts. The effect of variation of temperature on the solubility of different substances is very clearly shown by Gay Lussac's diagram of solubilities.

Water is by no means the only liquid which forms solutions of solids, although it is by far the most useful and general solvent. There is often observable some similarity of composition between the solvent and the dissolved body, water dissolving salts, acids, alcohols, but not hydrocarbons and fats. Hydrocarbons and fats are easily dissolved by hydrocarbons, as benzene ; phosphorus is readily soluble in phosphorus trichloride ; sulphur in carbon disulphide ; chlorine in chloroform. We cannot, however, foretell whether a certain solid will be dissolved or not by a given liquid although the composition of both be known, much less can we give any idea of the amount. We have, however, some relationships, as in the solubilities of the sulphates of barium, strontium, and calcium, of which the first is practically insoluble, and the last is the most soluble, and is the usual cause of the permanent hardness of natural waters. The hydrates of these three metals are much more soluble, but in just the reverse order.

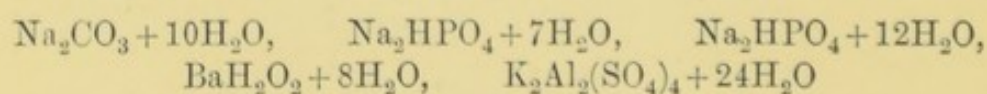
The elective nature of the mutual action of solvent and dissolved solid at once suggests the question, Is a

solution due to chemical combination between the two reacting substances? That this may be so is further rendered probable from the definiteness of the amount dissolved under definite conditions.

The older chemists undoubtedly regarded the act of solution as one of chemical change. They regarded the tendency to dissolve as a force to which the cohesion between the particles of the solid was antagonistic. An absolutely insoluble substance—if such exists—would be one in which the tendency to dissolve in a given liquid would be as nothing to the force of cohesion between its particles, and the varying solubilities of various substances would be due to the relative magnitudes of these forces. Since heat, as a general rule, tends to weaken cohesion, so therefore ought heat to promote solubility; and the higher the temperature we ought to have greater solubility, supposing the attraction between the solvent and the solid to remain the same.

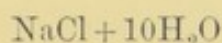
So far, then, this agrees with the facts observed. As the liquid dissolves more and more of the solid the attraction becomes less and less, till we have the two opposing forces balanced, and *saturation* results. This equilibrium is destroyed, as above indicated, by rise of temperature, but after a time a new condition of equilibrium results, and so on.

In very many cases we have been able to isolate definite compounds of solvent and solid, as is the case with many crystallised and hydrated salts, as



The two forms of sodium phosphate are obtained by

allowing solutions to crystallise at different temperatures, and so we may obtain hydrated crystals of many salts usually anhydrous by lowering sufficiently the point of crystallisation. Common salt, for example, is usually anhydrous, but by cooling brine to -23°C . we get crystals of



Crystals of this kind, which can only retain the water in the solid form at low temperatures, are known as *cryohydrates*. Even although we may obtain crystals containing both the solid and the solvent, it does not prove that in the solution they exist combined.

At the present time a vigorous discussion is going on as to what is the real condition of a substance when dissolved in a liquid. The rival theories are known as the "hydrate theory" and the "dissociation theory" of solution. The former regards solutions as consisting of definite compounds of solvent and the dissolved substance; the latter regards the dissolved substance as broken up in many cases into two parts, which remain in the solution together, but uncombined.

The hydrate theory is a simple one, and one of which it is not very easy to give any definite proofs, as any change of property is, when we come to dilute solutions, only very slight; and even if we are able to prove the existence of definite crystalline compounds, it by no means follows that these exist in the liquid state; nor, on the other hand, does the inability to obtain such prove that the solution is not a chemical compound of solvent and dissolved substance. We shall, therefore, consider first the "dissociation theory" of Arrhenius,

and see how it bears upon and explains the phenomena of solutions, especially of ordinary metallic salts.

This theory certainly introduces, at first sight, what seem to be highly improbable conditions, according to our generally received ideas of the stability of chemical compounds. It asserts, for instance, that when we dissolve common salt in water, it breaks up to a very large extent into sodium and chlorine ions, the sodium not acting on the water, nor the chlorine giving any evidence of its presence by smell or bleaching action. To entertain such an idea for a moment we must require some very powerful arguments, supported by clear experimental evidence of a conclusive nature.

In the previous chapters we have referred to various phenomena presented by matter in the liquid state, such as diffusion, lowering of freezing-point, change of tension of liquids when containing dissolved matter, &c. A complete theory should be able to account for these, and to explain any exceptions to the general rules established. In fact, it is by the study of such exceptions we very frequently obtain not only our clearest ideas, but even our first suggestions as to the true reasons for many phenomena.

If we take a narrow-necked bottle, cut off the bottom, and tie over in its place a porous membrane, fill the bottle with a solution of salt or sugar, fit tightly into the neck a cork and narrow tube, and immerse the whole in pure water, so that the level is the same inside and out, we see the level of the liquid rising in the tube, and this will go on till a very considerable pressure is attained. To be able to measure the maximum pressure we must use a porous vessel such as we use for

galvanic batteries, after having filled its pores with some colloid substance, such as copper ferrocyanide. This is readily done by filling the jar first with a solution of copper sulphate until the pores are filled with the solution, then washing it out carefully with water, and then by repeating the process with a solution of potassium ferrocyanide we get the pores filled with colloidal copper ferrocyanide. Such a cell will allow pure water to pass through it, but not dissolved matter such as sugar, and a solution of sugar, when placed inside, will require a much greater pressure to be applied to it than to pure water to filter pure water through it. The pressure required is, however, very definite, and may be determined thus:—Close the cell thus prepared with a stopper, and connect it with a manometer, and immerse it, after filling it with a solution of sugar, in pure water, an increase in pressure will be observed, which will go on until a definite maximum is reached, and this will depend directly on the strength of the sugar solution inside the cell if the temperature be kept constant. If the temperature be allowed to rise the pressure will increase at the same rate as the pressure of a gas increases when kept at constant volume. In fact, the *osmotic pressure*, as it is termed, varies directly as the absolute temperature of the solution. Not only does the pressure vary in the same way as a gas with regard to temperature, but we find that “the osmotic pressure of a sugar solution has the same value as the pressure that sugar would exert if it were contained as a gas in the same volume as is occupied by the solution.”

If we enunciate Avogadro's law thus: “Under equal conditions of temperature and pressure equal volumes of

all gases contain the same number of molecules," it is quite obvious we may write van't Hoff's law, given above, in a similar way, viz.: "Under equal osmotic pressures and at the same temperature equal volumes of solutions contain an equal number of dissolved molecules." Now, we had several well-marked exceptions to Avogadro's law, such as the vapours from ammonium chloride, sulphuric acid, and chloral hydrate. When we volatilise these we get twice the volume we should expect at ordinary pressure, or for a given volume we get twice the pressure. Now, when we dissolve such a salt as potassium chloride, we find that it gives an osmotic pressure very nearly twice as great as the above law leads us to expect. The exceptions are very numerous, and are in the majority of cases salts, acids, or bases. One property they have in common is that all are electrolysable. It is now long since Williamson and Clausius suggested that it was highly probable that electrolytes existed, to a certain extent at least, as free ions. Now, according to Arrhenius, the transport of electricity through a liquid is entirely brought about by means of these free ions, which each can take a definite charge of electricity, positive or negative, from the one electrode to the other. Potassium chloride in dilute solution, then, is supposed to exist there as potassium and as chlorine atoms, quite free from one another. Why does the potassium not decompose the water and liberate hydrogen from it? The potassium is prevented from doing so by its enormous charge of electricity. When, however, we place a solution in a vessel with electrodes and pass in a current, the potassium and the chlorine move in opposite directions, giving up their charge and

becoming the ordinary "free" element, as we know it at each electrode. The ions behave as if they had all the same capacity for electricity, hence we have Faraday's law, which states that "equal quantities of electricity require equivalent quantities of the ions for their transport." If we arrange several voltameters with solutions of sulphuric acid, silver nitrate, stannous chloride, bismuth nitrate, stannic chloride, and pass the same current on through them in series, we get for 1 part by weight of hydrogen liberated, 108 parts of silver, 59 of tin (from stannous salts), 69 of bismuth, and $29\frac{1}{2}$ of tin (from stannic salts); at the same time we obtain $35\frac{1}{2}$ of chlorine, 62 of the nitric acid radical (NO_3), and 48 of the radical of sulphuric acid (SO_4).

Further, electrolytes are substances of great chemical activity, and this is due to the dissociated state in which they exist, those substances which exist thus being obviously in a better condition to react. When we consider the ordinary reactions which we employ as qualitative and quantitative tests, we find in many cases that it is testing not for an element alone, unless it exists as an ion. For instance, in testing for chlorine with silver nitrate, we may have much chlorine present, and yet obtain no evidence of its presence by this test. Potassium chlorate solution mixed with that of silver nitrate gives no trace of silver chloride if pure, but if a trace of the chloride be present, we instantly have a white precipitate formed. The ions in this case are K and ClO_3 . Again, if we take a substance as analogous as possible to potassium chloride, but which does not admit of electrolysis because it does not dissociate in aqueous solution, such as ethyl chloride, we find it is

without action on silver nitrate. When one began to learn chemistry, one of the tests, which seemed to be a very odd one, was to use potassium ferrocyanide, a substance containing iron, to test for the presence of iron elsewhere. Yet the iron in this substance is not recognisable by any ordinary test for the metal either in the ferrous or ferric state. We get no reaction with ammonium sulphide, potassium hydrate, or ammonia. In solution it exists as the ions $4K$ and (FeC_6N_6) .

But sometimes we have with the same ion very different reactions, as iron in ferrous and ferric compounds, copper in cuprous and cupric compounds, and the radical (FeC_6N_6) of the ferrocyanides and of the ferricyanides. This is due to the different charges of electricity they bear. Their valency is proportional to their electrical charge.

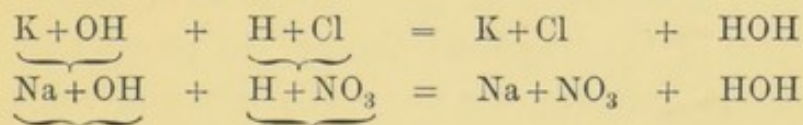
If the ability of a substance to enter into chemical reactions depends on the number of free ions it contains, and if its electric conductivity depends on exactly the same condition, it is very evident how it was possible for Ostwald to determine the coefficients of affinity from the electric conductivity of solutions.

On page 59 we gave Raoult's method of determining the molecular weights of substances in solution, and pointed out the abnormal behaviour of the aqueous solutions of salts, acids, and bases. We might here state the law in another form, viz., dilute solutions which contain an equal number of dissolved molecules in equal volumes of the same solvent have the same freezing-point. If, however, the substance dissociates as above supposed, we ought to have a much greater lowering in the case of electrolytes than in non-electro-

lytes. For normal solutions of sugar and of potassium chloride the freezing-points are respectively $-1^{\circ}89$ C. and $-3^{\circ}5$ C.

In the same way, the volume changes produced on neutralisation, to which we referred in the last chapter, and which were also used by Ostwald to determine coefficients of affinity, lead exactly to the same conclusions as to the nature of solutions.

This view of the nature of solutions explains clearly why there should be no evolution of heat on mixing two solutions, as Hess pointed out was the case in enunciating his law of thermo-neutrality, for in each solution we have very little decomposable matter, the salts present being there mainly as free ions. It also gives the reason for the evolution of heat being almost exactly the same when strong acids and bases neutralise one another—



the actual combination taking place between $\text{H} + \text{OH}$ to form H_2O .

The "hydrate theory" is held by many well-known chemists, and certainly requires at first sight much fewer startling assumptions than the other. The proofs of hydrates existing even in extremely dilute solutions are deduced from the study of the amount of heat evolved in the solution of sulphuric acid, for example, in varying quantities of water. If we use the graphic method of comparing these amounts of heat by plotting the amounts as ordinates and the percentage composition of the solution as abscissæ, the curve produced is not a

uniform one, but indicates the presence of compounds by sudden changes of direction. Conductivity, density, and refractive index may be used, and seem to give similar results.

We might pursue the analogy between a solid dissolving and a solid dissociating, or a liquid vaporising, still further. A liquid volatilises until a definite pressure is reached, depending on the temperature alone; in the same way a solid dissolves to a certain extent, which is likewise dependent on the temperature; and just as liquids exert very different pressures at a uniform temperature, so do solids have very different solubilities, and consequently have very different osmotic pressures at the same temperatures.

The "osmotic pressure" or "dissociation theory" of solution accounts for so many hitherto unexplained facts that the burden of proof seems to be laid on the upholders of the "hydrate theory" to prove that it is wrong. It only requires one really new and somewhat startling change as to our ideas regarding chemical stability in solution, and is supported by so many experimental data correlating almost all the phenomena of solution in such a marvellous manner that one feels bound to admit its truth.

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