INORGANIC CHEMISTRY

PART I

INTRODUCTORY OUTLINES

CHAPTER I

CONSTITUTION OF MATTER

THE science of chemistry may be described as the study of a certain class of changes which matter is capable of undergoing. Matter is susceptible of a variety of changes, some of which are regarded as *physical* and others as *chemical*. Thus, when a steel knitting-needle is rubbed upon a magnet, the needle undergoes a change, by virtue of which it becomes endowed with the power of attracting to itself iron filings or nails; and when an ordinary lucifer match is rubbed upon a match-box the match undergoes a change, resulting in the production of flame. In the first case the change is said to be a *physical* one, while the ignition and combustion of the match is a *chemical* change.

When a fragment of ice is gently warmed, it is changed from a hard, brittle solid to a mobile, transparent liquid; and when white of egg is gently heated, it changes from a transparent, colourless liquid to an opaque white solid. These changes, which appear at first sight to be of a similar order, are in reality essentially different in their nature: the transformation of solid ice into liquid water is a *physical* change, the coagulation of albumen is a *chemical* change.

Again, when certain substances (such as the materials which constitute the so-called *luminous paint*) are exposed to a bright light, they undergo a change whereby they become invested with the power to emit a feeble light when seen in the dark. A stick of phosphorus also emits a very similar light when seen in the dark. The glowing of these materials under these circumstances might readily be regarded as the result of the same kind of change in both cases; but in reality the luminosity of the phosphorus is due to a *chemical* change taking place upon the surface of that substance, while the emission of light from the luminous paint is a purely *physical* phenomenon.

The two sciences, chemistry and physics, are so closely related and interdependent upon each other, that no sharp distinction or line of separation between them is possible. Every *chemical* change that takes place is attended by some *physical* change, and it often happens that this accompanying physical change forms the only indication of the chemical change that has taken place. In certain important points, however, a chemical change is very different from one that is purely physical: in the latter case no material alteration in the essential nature of the substance takes place. This will be seen in the examples quoted. The steel needle remains unaltered in its essence, although by magnetisation it has acquired a new property—a property which it again loses, and which can be again and again imparted to it. The match, on the other hand, when ignited has undergone a material and permanent change: the combustible substance is now no longer combustible, neither will it ever return to its original state. The solid water, in being transformed to liquid water, has not undergone any vital change; in essence it is the same substance merely endowed with a new property of liquidity, a property which it loses again when cooled, and which can be again and again imparted to it. On the other hand, the coagulated albumen has undergone a complete and lasting change, and never returns to its original condition.

In the same way, the luminous paint gradually ceases to emit light, and returns to its original state; it may be exposed to the influence of light, when it once more acquires the property of phosphorescence, and this change may be brought about indefinitely, without altering the intrinsic nature of the substance. The glowing phosphorus, on the other hand, is gradually changed into a white substance, which escapes from it as a smoke or fume; in the act of glowing the phosphorus is undergoing a process of slow burning, and if allowed to remain will continue glowing and burning until the whole of it has disappeared in the form of smoke.

The Constitution of Matter. Molecules.—Matter is regarded by the chemist and physicist as being composed of aggregations of minute particles; every substance, whether it be solid, liquid, or gaseous, presents the appearance to his mind of a vast number of extremely minute particles. To these particles the name molecules ("little masses") has been given. The particles or molecules of any particular substance are all alike: thus in sulphur the molecules are all of one kind, while in water they are all of another kind; the chemical properties associated with sulphur are the properties of the individual sulphur molecules, while those belonging to water are the properties of the molecules of that substance. All matter, therefore, is to be conceived as having what may be called a *grained* structure. The actual sizes of molecules is a matter which has not yet been determined with exactness; they are orders of magnitude which are as difficult for the mind to grasp on account of their minuteness, as many astronomical measurements are by reason of their vastness. It is certain that their size is less than half a single *wave-length* of light,* and that therefore they are beyond the visual limits of the microscope. Some general idea of their order of magnitude may be gathered from Lord Kelvin's calculation, that if a single drop of water were magnified to the size of the earth, each molecule being proportionately enlarged, the grained appearance which the mass would present would probably be finer than that of a heap of cricket-balls, but coarser than a heap of small shot.

It will be evident, therefore, that in the strictest sense matter is not *homogeneous*, since it consists of aggregations of molecules, between which there exist certain interspaces.

The forces which similar molecules exert upon each other are regarded as *physical*, in contradistinction to *chemical*. These forces are either *attractive* in their nature, or *repellent*. The attractive forces tend to draw the molecules closer together, and thus to cause the substance to assume the solid state; while repellent forces, on the other hand, tend to separate the molecules and to make the substance pass into the gaseous condition. Changes which matter undergoes by the action of these forces are *physical* changes; they do not affect the chemical nature and properties of the substance, which properties, as already stated, reside in the molecules themselves.

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* The wave-length of the blue ray (G) = 0.0004311 millimetre, or 0.0000169 inch.

In each of the three states of matter, viz. solid, liquid, or gaseous, the molecules are conceived as being in a state of motion; they are regarded as executing some vibratory movement within the spaces that divide them. In the solid state this movement is usually the most restricted, for the reason that in this case the intermolecular spaces are as a rule the smallest. In the gaseous condition, however, the attractive force between the molecules has been almost entirely overcome by the operation of the repellent forces. The molecules are therefore widely separated, and consequently permit of a much greater freedom of movement.

Such changes in matter, which are merely the result of alterations in the motions of the molecules, are likewise purely *physical changes.*

Molecules may be defined as *the smallest particles of matter which can exist in the free state;* or as *the smallest weight of matter in which the original properties of the matter are retained.*

Atoms.—It is the belief of chemists that most molecules are possessed of a *structure.* That is to say, they are not simple, single, indivisible masses, but themselves consist of aggregations of still smaller particles, which are held together by the operations of some other force. These particles of which molecules are composed are termed atoms, and the force which holds them together is called chemical affinity, or chemical attraction. To the mind of the chemist, such molecules are little systems, consisting of a number of atoms which are attracted to each other by this particular force; in the ordinary movements of the molecule, the system moves about as a whole. In this respect it bears some analogy, on an infinitely minute scale, to a solar system. The atoms of a molecule are regarded as in a state of motion as respects one another, possibly revolving about one another, while the entire system, or molecule, at the same time performs its independent movements, just as in a solar system the various members perform various movements towards each other, while at the same time the whole system travels upon its prescribed orbit. In the case of the heavenly bodies, the force which regulates the movements of the individual members of the system amongst themselves is the same force that controls the motion of the united system, namely, gravitation. What is the precise relation, or difference, if any, between the forces which control the movements of molecules, and those which operate between the atoms of the molecule, is not known; but as the effects produced are different, the latter force is distinguished by the name of chemical affinity.

Any change which matter undergoes, in which the integrity of the molecules is not destroyed, is regarded as a physical change; while any change which arises from an alteration in the structure of the molecule is a chemical change. For example, the molecules of water consist of three separate atoms, one of oxygen and two of hydrogen; any change which water can be made to undergo, in which these three atoms still remain associated together as the molecule, is a physical change. The water may be converted into ice, or it may be changed into steam; but these alterations still leave the molecules intact—the three atoms still remain united as an unbroken system, and so long as this is the case chemical change has not taken place.

Suppose now the molecules of water are heated to a much higher temperature than that which is necessary to convert the water into steam, by passing electric sparks through the steam. It will then be found that a very different kind of change has come over the substance. The steam, after being so heated, no longer condenses to water again when cooled; it has been changed into a gas which can be bubbled through water and collected in an inverted vessel filled with water standing in a pneumatic trough, and if a flame be applied to this gas a sharp explosion takes place. The change in this case is a chemical change, for the integrity of the molecules of water has been destroyed. The two atoms of hydrogen have become detached from the oxygen atom, and the original triune structure of the system is destroyed.

Atoms are therefore defined as *the smallest particles of matter which can take part in a chemical change.*

CHAPTER II

ELEMENTS AND COMPOUNDS

THERE are certain molecules in which all the atoms present are of the same kind, and there are other molecules which are composed of atoms which differ from one another. Thus, in the substance sulphur, all the atoms composing the molecules are alike; while in water, as already mentioned, there are two distinct kinds of atoms in the molecule. Matter, therefore, is divided into two classes, according as to whether its molecules are composed of similar or of dissimilar atoms. Molecules consisting of atoms of the same kind are termed *elementary molecules*, and substances whose molecules are so constituted are known as elements; molecules, on the other hand, which contain dissimilar elements are called *compound molecules*, and substances whose molecules are thus composed are distinguished as compounds.

Sulphur, therefore, is an *element*, and water is a *compound*. It will be evident that in the case of elementary molecules, whatever processes they may be subjected to, only one kind of matter can be obtained from them; while in the case of compounds, the molecules consisting of dissimilar atoms, as many different kinds of matter can be obtained as there are different atoms present. By appropriate means the atoms of hydrogen and oxygen in water molecules can be separated, and two totally different kinds of matter, namely, hydrogen and oxygen, can be obtained from this compound.

At the present time there are about seventy substances known to chemists which are believed to be elements. In the history of the science it has frequently happened that substances which were considered to be elements have proved, when subjected to new methods of investigation, to be in reality compound bodies: thus, prior to the year 1783, water was thought to be an elementary substance; it was indeed regarded as the very type of an element, until Cavendish and Lavoisier proved that it was composed of two entirely different kinds of matter. In the year 1807 Sir

Humphry Davy showed that the substances known as potash and soda, which were believed to be elements, were in reality compound bodies, and he succeeded in separating the constituent atoms in the molecules of these substances, and in obtaining from them two essentially different kinds of matter. It is therefore quite possible, perhaps even probable, that some at least of the forms of matter which are now held to be elements may yet prove to be compound bodies. On the other hand, the list is from time to time extended by the discovery of new elements. Thus during the last few years at least five new members have been added to the number.

The number of compounds is practically infinite.

The elements are very unequally distributed in nature, and are of very different degrees of importance to mankind. Some are absolutely essential to life as it is constituted, while others might be blotted out of creation without, so far as is known, their absence being appreciated. The following thirty elements include all the most important (for the complete list see page 22) :—

Aluminium.
Antimony.
Arsenic.
Bismuth.
Bromine.
Calcium.
Carbon.
Chlorine.
Copper.
Fluorine.
Gold.
Hydrogen.
Iodine.
Iron.
Lead.
Magnesium.
Manganese.
Mercury.
Nickel.
Nitrogen.
Oxygen.
Phosphorus.
Platinum.
Potassium.
Silicon.
Silver.
Sodium.
Sulphur.
Tin.
Zinc.

On account of certain properties common to a large number of the elements, and more or less absent in others, properties which are for the most part physical in character, the elements are divided into two classes, known as *metals* and *non-metals*. The metals generally are opaque, and their smoothed surfaces reflect light to a high degree, thus giving them the appearance known as *metallic lustre*. They also conduct heat and electricity. Gold, silver, copper, iron, are metals; sulphur, bromine, oxygen, phosphorus, are non-metals. These two classes, however, gradually merge into one another, and certain elements are sometimes placed in one division and sometimes in the other, depending upon whether the distinction is based more upon their physical or their chemical properties: thus, the element arsenic possesses many of the physical properties of a metal, but in its chemical relations it is more allied to the non-metals; such elements as these are often distinguished by the name *metalloids.* The following list embraces all those elements which by common consent are regarded as non-metals and metalloids, including the recently discovered elements of the argon group, which are here printed in italics:—

Arsenic.
Boron.
Bromine.
Carbon.
Chlorine.
Fluorine.
Hydrogen.
Iodine.
Nitrogen.
Oxygen.
Phosphorus.
Selenium.
Silicon.
Sulphur.
Tellurium.
Helium.
Neon.
Argon.
Krypton.
Xenon.

The number of atoms which compose the various elementary molecules is not the same in all cases; thus in the elements sodium, potassium, cadmium, mercury, and zinc, the molecules, when the elements are in a state of vapour, consist of only one atom. The same is true also of the newly discovered elements in the last column. The molecules of all these substances are single particles of matter. The terms *molecule* and *atom*, therefore, as applied to these elements, are synonymous. Such molecules as these are called *mono-atomic* molecules. In many cases elementary molecules consist of two atoms; such is the case with the elements hydrogen, bromine, chlorine, oxygen, nitrogen, and others. Elementary molecules of this twin or dual nature are known as *di-atomic* molecules. Only one instance is known in which an elementary molecule consists of a trio of atoms, namely, the molecule of ozone, which is an aggregation of three oxygen atoms. This molecule is said to be *tri-atomic.* In two cases, namely, arsenic and phosphorus, the molecules are composed of a quartette of atoms, and these elements, therefore, are said to form *tetr-atomic* molecules. In a large number of instances the atomic constitution of the molecule of the elements is not known. These terms, *mono-atomic*, *di-atomic*, &c., are applied exclusively to molecules of *elements*, and are not used in reference to compounds, where the molecules are composed of dissimilar atoms.

Mechanical Mixtures.—When molecules of different kinds of matter are brought together, one of two results may follow: either they will merely mingle together without losing their identity, that is to say, the atoms composing the individual molecules will still remain associated together as before, or the atoms in the molecules of one kind will attach themselves to certain atoms present in molecules of another kind to form still different molecules ; in other words, there will be a redistribution of the atoms, whereby different systems or molecules are produced.

In the first case the result is said to be a simple or mechanical mixture, in the second it is the formation of a chemical compound.

In a simple *mixture* the ingredients can be again separated by purely mechanical methods ; and as the properties of a substance are the properties of the molecules of that substance, it follows that if the integrity of the molecules is not broken, the properties of a mechanical mixture will be those of the ingredients. For example, oxygen is a colourless gas without taste or smell ; hydrogen also is a colourless gas without taste or smell : when these two gases are mixed together, the mixture is gaseous, is colourless, and tasteless, and, being only a mixture, the molecules of one gas can be readily sifted away from the other.

Again, charcoal is a black solid, insoluble in water ; sulphur is a yellow solid, also insoluble in water ; nitre is a white solid, readily dissolved by water : when these three substances are finely powdered and mixed together, the result is a mechanical mixture, which is solid, and which is dark grey or nearly black in colour. If this mixture be placed in water, the nitre is dissolved away and the charcoal and sulphur are left.

When, however, the integrity of the molecules is disturbed, and a rearrangement of the atoms takes place, resulting in the formation of new molecules, then it is said that chemical action has taken place.

Chemical action, therefore, always results in the formation of new molecules—new molecules which are endowed with their own special properties, differing often in the most remarkable and quite inexplicable manner from those of the original molecules. One or two examples may be quoted in order to illustrate this extraordinary modifying effect of chemical action. The two colourless gases, oxygen and hydrogen, when simply mixed together, give rise, as already mentioned, to a colourless, gaseous mixture, in which the dual molecules of hydrogen and the similarly constituted oxygen molecules move about freely amongst each other. By suitable means chemical action may be made to take place between these two elements, whereby a complete rearrangement of the atoms takes place, resulting in the formation of molecules of water—molecules in which, as has been already mentioned, one atom of oxygen is associated with two atoms of hydrogen. The product of the chemical action is therefore water, while both the forms of matter of which it is composed are gaseous.

The air we breathe, and which is necessary to life, consists of a simple mixture of two colourless gases, viz., oxygen and nitrogen. When chemical action takes place between these substances, a brown-coloured gas is produced in which no animal or vegetable life could exist for many minutes, on account of its suffocating nature.

Common salt, which is a white solid substance, and not only harmless, but even a necessary article of food, contains two atoms in its molecules—one an atom of chlorine, and the other an atom of sodium. Chlorine is a yellow gas, intensely suffocating and poisonous; and sodium is a soft, silver-like metal, which takes fire in contact with water.

Why it is that a molecule, consisting of an atom of chlorine and an atom of sodium held together by chemical affinity, should be endowed with properties so totally different from those of the contained elements, is altogether unknown; and similarly, it is quite impossible to predicate from the properties of any compound what are the particular elements of which it is composed. Thus, sugar is a white crystalline solid, soluble in water, and possessing a sweet taste; but no one would have ventured to predict that the molecules of this substance were composed of atoms of *carbon*, a black, tasteless, insoluble solid; *hydrogen*, a colourless, tasteless gas; and *oxygen*, another colourless, tasteless gas.

Chemical Affinity.—When molecules, consisting of two atoms, say A B, come in contact with molecules consisting of other two atoms, C D, and a chemical change takes place resulting in the formation of new molecules, A C and B D, the question naturally arises, Why does the atom A leave the atom B and attach itself to C? In other words, what determines the rearrangement of the atoms into new molecules?

At present no exact answer can be given to this question. Chemists express the fact by saying that the chemical affinity existing between A and C is greater than that exerted by B upon A. This remarkable selective power possessed by the atoms of different elements lies at the root of all chemical phenomena, and it differs between the various elements to an extraordinary degree. For example, the atom of chlorine possesses a very powerful chemical affinity for the atom of hydrogen : when hydrogen molecules, which consist of two atoms, are mixed with chlorine molecules, which are also aggregations of two atoms, at first a simple mechanical mixture is obtained, the two different kinds of molecules move amongst each other without undergoing change. On very small provocation, however, the affinity of the hydrogen atoms for the chlorine atoms can be caused to exert itself; by merely momentarily exposing the mixture to sunlight a complete redistribution of the atoms suddenly takes place with explosive violence and new molecules are formed, each containing one atom of hydrogen and one atom of chlorine.

Again, an atom of nitrogen is capable of associating itself in chemical union with three atoms of the element chlorine, forming a compound whose molecules therefore contain four atoms. The chemical affinity between the atoms of chlorine and nitrogen is so feeble, the system is, so to speak, in a state of such unstable equilibrium, that the very slightest causes are sufficient to instantly separate the atoms in the most violently explosive manner, and so break up the compound molecules into separate molecules of chlorine and nitrogen. In this case the affinity between one chlorine atom and another chlorine atom is greater than that between chlorine and nitrogen, consequently the redistribution that results is of the opposite order to that of the former example.

As a rule, those elements which the more closely resemble each other in their chemical habits have the least affinity for each other, while the greatest affinity usually exists between those which are most dissimilar.

Chemical Action.—The actual process of redistribution of the atoms that takes place when molecules of different kinds of matter are brought together is called *chemical action.* In many cases chemical action takes place when the substances are merely brought together, while in others it is necessary to expose the bodies to the influence of some external energy : thus chemical action is brought about in a great number of instances by the application of heat to the substances. In some cases the influence of light has the effect of causing chemical action to take place; for example, when the gases chlorine and hydrogen are mingled together, no chemical action takes place in the dark, but on exposing the mixture to light the hydrogen and chlorine combine, and form the compound hydrochloric acid. It is upon the effect of light in causing chemical action to take place that the art of photography depends.

Chemical action may sometimes be induced by the influence of pressure; thus, when the two gases, hydrochloric acid and phosphoretted hydrogen, are subjected to increased pressure they combine together to form a crystalline solid compound known as phosphonium chloride. In the same way, by very great mechanical pressure, a mixture of powdered lead and sulphur can be caused to combine together, when they form the compound, lead sulphide. There are also a number of chemical actions that are only able to proceed in the presence of small quantities (often *extremely* small) of a third substance, which itself remains unchanged at the conclusion of the action. These cases are generally included under the name of *catalytic* actions: in some of them the *modus operandi* of the third substance can be traced (see Oxygen, Modes of Formation; also Chlorine, Deacon's Process), while in others it is not understood. Thus it is found that a number of chemical actions are quite unable to take place if the materials are *absolutely* dry; for example, the element chlorine has a powerful affinity for the metal sodium, and when these substances are brought together under ordinary conditions, chemical action instantly takes place, and the compound known as sodium chloride (common salt) is produced. If, however, every trace of moisture be perfectly removed from both the sodium and the chlorine, no action between these elements takes place when they are brought together, and so long as they remain in this state of perfect dryness no chemical change takes place. The admission into the mixture of the minutest trace of the vapour of water, however, at once induces chemical action between the chlorine and the sodium, but the exact part that the trace of moisture plays in producing this effect is not known with certainty. (See also foot-note, page 89.)

A few interesting cases are known in which chemical action is brought about by the vibration caused by a loud sound or note; for example, the molecules of the gas acetylene consist of two atoms of carbon associated with two of hydrogen. When a quantity of this gas is exposed to the report produced by the detonation of mercury fulminate, the mere shock of the explosion causes a redistribution of the atoms whereby solid carbon is deposited and hydrogen set free. We may suppose that the particular vibration produced by the detonation of the fulminate exercises a disturbing effect upon the motions of the atoms constituting the molecules of acetylene, and thereby causes them to swing beyond the sphere of their mutual attractions, and thus the system undergoes disruption and rearrangement.

All known instances of chemical action can be referred to one of three modes, in which the rearrangement of the atoms can take place.

(1.) *By the direct union of two molecules to form a more complex molecule.* Thus, if CO and ClCl represent two molecules between which chemical action takes place according to this mode, they unite to form a molecule containing the four atoms COClCl.

(2.) *By an exchange of atoms taking place between different molecules.* In its simplest form this is illustrated in the action of one element upon another to form a compound. Thus, if HH and ClCl stand for two elementary molecules between which chemical action takes place, the result is the formation of the two molecules HCl HCl. Such a process as this, in which a compound substance is produced directly from the elements which compose it, is termed *synthesis.*

The same mode of chemical action may also be exemplified by the exact opposite to this process, namely, the resolution of a compound into its constituent elements. Thus, if OHH OHH represent two molecules of the same compound, when chemical action takes place it will result in the formation of the three elementary molecules OO, HH, and HH. Such a process as this, in which a compound is resolved into its elements, is known as *analysis.**

(3.) *By a rearrangement of the atoms contained in a molecule.* There are a number of instances of chemical change, in which the molecules of the substance do not undergo any alteration in their *composition*—that is to say, no atoms leave the molecule, nor are any added to it. The molecule still consists of the same atoms after the change as it did before, but the chemical action has

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* It will be seen that in each of the examples here given, the process of rearrangement involves first the decomposition of one or both of the reacting molecules, and then the combination of the atoms to form different molecules.

caused them to assume new relative positions, or different relative motions with respect to each other. For example, the substances known to chemists as *ammonium cyanate* and *urea* are two totally different and distinct kinds of matter. These molecules, however, each contain the same atoms and in the same number; they each consist of aggregations of one atom of carbon, one atom of oxygen, two atoms of nitrogen, and four atoms of hydrogen. When ammonium cyanate is gently warmed, the eight atoms composing the molecules undergo this process of rearrangement, and the substance is changed into urea.

When chemical action takes place between two substances, say A and B, in ordinary language we say that A acts upon B. Such a statement, however, must not be understood to imply that A takes the initiative, so to speak, and that B is in any way less responsible for the action. It is equally true to say that B acts upon A. For instance, we commonly say nitric acid acts upon copper, hydrochloric acid acts upon zinc, nitric acid has no action upon gold, and so on; but it is equally true to say copper acts upon nitric acid, zinc acts upon hydrochloric acid, gold has no action upon nitric acid. A more strictly scientific expression would be A and B react, or do not react, as the case may be. Thus, nitric acid and copper react, gold and nitric acid do not react.

CHAPTER III

CHEMICAL NOMENCLATURE

THE names which have been given to the various elementary forms of matter are not based upon any scientific system. The names of some have their origin in mythology. Others have received names which are indicative of some characteristic property, while those of several bear reference to some special circumstance connected with their discovery. It has been the custom in modern times to distinguish metals from non-metals by applying to the former names ending in the letters *um*, and consequently such metals as are of more recent discovery all have names with this termination. The common metals, however, which have been known since earlier times, such as gold, silver, tin, and copper, keep their old names. The two elements selenium and tellurium were at the time of their discovery thought to be metals, and they consequently received names with the terminal *um*; these substances strongly resemble metals in many of their physical properties, but in their chemical relations they are so closely similar to the non-metal sulphur, that they are by general consent classed among the non-metals; they are examples of those elements which are distinguished as metalloids. On this account selenium is by some chemists termed *selenion.*

In naming chemical compounds, the chemist endeavours that the names employed shall not only serve to identify the substances, but shall as far as possible indicate their composition. The simplest chemical compounds are those composed of only two different elements; such are spoken of as *binary compounds*,* and their names are made up of the names of the two elements composing them, thus—

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* This expression is now sometimes used in a somewhat modified sense. Thus in the language of the ionic theory (p. 107) the term *binary compound* is used to denote a substance which dissociates into *two ions*, quite irrespective of the number of elements it may contain. It is to be regretted that under these circumstances a new word was not coined to denote the newer idea.

The compound formed by the chemical union of—

Hydrogen with sulphur is called hydrogen sulphide.
Sodium ,, chlorine ,, sodium chloride.
Copper ,, oxygen ,, copper oxide.
Calcium ,, fluorine ,, calcium fluoride.
Potassium ,, iodine ,, potassium iodide.

It continually happens, however, that the same two elements combine together in more than one proportion, giving rise to as many different compounds, in which case it becomes necessary to so modify the names that each of the compounds may be distinguished. This is accomplished by the use of certain terminal letters or of certain prefixes; for example, the element phosphorus combines with chlorine in two proportions, forming two different compounds—in one the molecules contain one atom of phosphorus united to three atoms of chlorine, in the other the molecules consist of one atom of phosphorus associated with five of chlorine. These two compounds may be distinguished in the following ways :—

1 atom of phosphorus with 3 atoms of chlorine forms phosphor*ous* chloride.
1 ,, ,, ,, 5 ,, ,, ,, phosphor*ic* chloride.

or—

1 atom of phosphorus with 3 atoms of chlorine forms phosphorus *tri*chloride.
1 ,, ,, ,, 5 ,, ,, ,, phosphorus *penta*chloride.

The latter method of distinction is the more general, thus—

1 atom of sulphur with 2 atoms of oxygen forms sulphur dioxide.
1 ,, ,, ,, 3 ,, ,, ,, sulphur trioxide.
1 atom of carbon with 1 atom of oxygen forms carbon monoxide.
1 ,, ,, ,, 2 atoms ,, ,, carbon dioxide.

Occasionally the prefixes *sub* and *proto* are employed to denote these differences of composition, but their use is more limited, and is becoming out of vogue. When more than two compounds are formed by the union of the same two elements, the additional prefixes *hypo*, under, and *per*, over, are sometimes used.

In a considerable number of instances the systematic names of familiar compounds give way to the vulgar or common names by which they are known, thus—

Common names	Systematic names.
Ammonia	Hydrogen nitride
Hydrochloric acid	Hydrogen chloride
Sulphuretted hydrogen	Hydrogen sulphide
Water	Hydrogen monoxide

Binary compounds that are formed by the union of elements with oxygen are called the *oxides* of those elements. Certain of these oxides are capable of entering into combination with water, giving rise to substances known as *acids;* such oxides are distinguished as *acid-forming oxides*, or *acidic* oxides. They are also sometimes termed *anhydrides.* All the non-metallic elements, except hydrogen and the members of the argon group, form oxides of this order, and the acids derived from them are known as the oxy-acids.

Certain other oxides also unite with water, but give rise to compounds known as *hydroxides.* When such oxides, which are all derived from the metallic elements, are brought into contact with acids, chemical union takes place, and a compound termed a *salt* is formed. Such oxides are distinguished as *salt-forming* or *basic* oxides. There are also oxides which are neither *acidic* nor *basic.* The names of oxy-acids are derived from the name of the particular oxide from which they are formed, thus—

Carbon dioxide gives carbonic acid.
Silicon dioxide „ silicic acid.

When the same element forms two acid-forming oxides, the terminals *ic* and *ous* are applied to the acids to denote respectively the one with the greater and the less proportion of oxygen, thus—

Sulphur *tri*oxide gives sulphur*ic* acid.
Sulphur *di*oxide gives sulphur*ous* acid.
Nitrogen *pent*oxide gives nitr*ic* acid.
Nitrogen *tri*oxide gives nitr*ous* acid.

When more than two such acids are known, the additional prefixes *hypo* or *per* are made use of. Thus *per*sulphuric acid denotes an acid containing the highest quantity of oxygen, while *hypo*nitrous acid stands for an acid containing less oxygen than is present in nitrous acid.

There is a class of binary compounds formed by the combination of a large number of the elements with sulphur; these are known as *sulphides.* Certain of these sulphides are also capable of forming acids which are analogous in their constitution to oxy-acids, but in which the oxygen atoms are substituted by atoms of sulphur. These acids are known as *thio* acids (sometimes *sulpho* acids), and the same system of nomenclature is adopted to distinguish these: thus we have thio-arseni*ous* acid, thio-arsen*ic* acid, denoting respectively the acid with the smaller and the larger proportion of sulphur.

It was at one time believed that all *acids* contained oxygen, that indeed this element was essential to an acid. The name *oxygen* indicates this belief, the word signifying "the acid-producer." This view is now seen to have been incorrect, for many acids are known in which oxygen is not one of the constituents. Thus the elements fluorine, chlorine, bromine, and iodine, which constitute the so-called Halogen group of elements, each combines with hydrogen, giving rise respectively to hydrofluoric, hydrochloric, hydriodic, and hydrobromic acids.

All known acids contain hydrogen as one of their constituents.

As already stated, when chemical action takes place between an acid and a base* a *salt* is formed. Oxy-acids in this way give rise to oxy-salts, thio-acids to thio-salts, and halogen acids to haloid salts.

The latter salts being *binary* compounds, their names are given according to the system already explained, such, for example, as calcium fluoride, sodium chloride, potassium bromide, silver iodide.

In the case of the oxy-salts and thio-salts, the names are made up from the names of the acid and of the metal contained in the base, with the addition of certain distinctive suffixes : thus if the acid be one whose name carries the terminal *ous*, its salts will be

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* The word *base* is unfortunately employed by different chemists in different senses, so that it is scarcely possible to give a precise definition of it. Originally, no doubt, the term was employed simply to denote the idea of *foundation*, and was applied to the metal or the oxide of the metal entering into the composition of a salt ; which being the more tangible constituent was thus regarded as the more important one, or the *basis* of the salt. At the present day the word base is used in INORGANIC chemistry chiefly to denote that class of compounds described on page 17 as *hydroxides*, while the oxides from which these hydroxides are derived are spoken of as *basic oxides*. Besides this class, it includes ammonia and a few other compounds which like ammonia are not derived from metallic oxides. The ORGANIC chemist, on the other hand, regards ammonia as the true type of a base ; and all organic compounds which can be regarded as "derivatives" of ammonia are called bases. Not only so, but the term is even extended so as to include similar "derivatives" of the phosphorus, arsenic and antimony analogues of ammonia, thus giving rise to the expressions *nitrogen bases*, *phosphorus bases*, &c.

Again, in the language of the modern theory of ionic dissociation, a base is defined as a compound in which the only negative ions are the *hydroxide* ions (page 107). This definition includes the class of hydroxides above mentioned, but does not include ammonia gas.

distinguished by the suffix *ite*, while the names of the salts derived from acids whose names end in *ic* are terminated by the letters *ate*.

Nitr*ous* acid and potassium oxide give potassium nitr*ite*.
Sulphur*ous* acid „ „ „ sulph*ite*.
Nitr*ic* acid „ „ „ nitr*ate*.
Sulphur*ic* acid „ „ „ sulph*ate*.

The formation of a salt by the action of an acid upon a base is due to the redistribution of the atoms composing the molecules of the two compounds, in such a manner that some or all of the hydrogen atoms in the acid molecules exchange places with certain metallic atoms from the molecules of the base. Acids which contain only one atom of hydrogen so capable of becoming exchanged for a metal are termed *mono-basic* acids ; those with two, three, or four such hydrogen atoms are distinguished respectively as *di-basic*, *tri-basic*, and *tetra-basic* acids.

If the whole of the displaceable hydrogen in an acid becomes replaced by the base, the salt formed is known as a *normal* salt. On the other hand, when only a portion of the hydrogen atoms is displaced by the base, the salt is distinguished as an *acid* salt. Thus sulphuric acid contains two atoms of hydrogen in its molecule (associated with one of sulphur and four of oxygen) ; if both the hydrogen atoms are exchanged for potassium, the salt obtained is *normal potassium sulphate*, and when only one is so replaced the salt is known as *acid potassium sulphate*. By the term *acid salt*, therefore, must be understood *not* a substance having the familiar properties of an acid, such as a sour taste and the power to redden litmus, but a salt in which one or more of the hydrogen atoms of the original acid are still left in the molecule.* It is quite true that some of the salts of this class do possess acid qualities and will redden litmus, but this is due to what may be regarded as merely the accidental circumstance of the *acidic* portion of the molecule being derived from a strong acid. Many substances belonging to the class of *acid salts* are perfectly neutral in their behaviour towards litmus, while, on the other hand, some are strongly alkaline. For example, *acid potassium sulphate* is acid

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* Some chemists prefer to regard the acids themselves as the hydrogen salts ; accordingly they apply to nitric acid, sulphuric acid, nitrous acid, sulphurous acid, &c., the names hydrogen nitrate, hydrogen sulphate, hydrogen nitrite, hydrogen sulphite, &c., respectively.

to test paper, *acid calcium carbonate* is neutral, while *acid sodium carbonate* is alkaline.

A third class of salts is formed by the association of one or more molecules of normal salt, with one or more additional molecules of the base : these are known as *basic* salts. Thus, carbonic acid and the base lead hydroxide form such a salt known as *basic lead carbonate.*

CHAPTER IV

CHEMICAL SYMBOLS

CHEMISTS are agreed in adopting certain symbols to denote the atoms of the various elementary forms of matter. The table on page 22 contains the names of the elements at present recognised, and in the second column are given the symbols which are employed to represent their atoms. The names of the rare elements are printed in italics.

In a number of instances the atomic symbol is the initial letter of the ordinary name of the element: thus Boron, B; Carbon, C; Fluorine, F; Hydrogen, H; Oxygen, O; Sulphur, S.

When more than one element has the same initial, either the first two letters of the name, or the first and another that is prominently heard in pronouncing the word are employed, as Bromine, Br; Cobalt, Co; Chlorine, Cl; Platinum, Pt. In some cases letters taken from the Latin names for the elements are used, such as Antimony (*Stibium*), Sb; Gold (*Aurum*), Au; Silver (*Argentum*), Ag; Lead (*Plumbum*), Pb; and Iron (*Ferrum*), Fe.

These symbols are not intended to be employed as mere shorthand signs, to be substituted as abbreviations for the full names of the elements, but in every case they denote one atom of the element. The symbol H stands for one atom of hydrogen, the symbol O stands for one atom of oxygen; Cl means one atom of chlorine, and Ag represents one atom of silver. No other use of these symbols is legitimate.

It has been already mentioned (page 8) that the molecules of the different elements are composed of different numbers of atoms; for example, the molecule of hydrogen consists of two atoms, and ordinary oxygen also forms diatomic molecules. These facts are expressed in chemical notation by the use of small numerals placed immediately after the symbol of the atom, thus H_2 denotes a molecule of hydrogen, O_2 a molecule of oxygen. The molecule of ozone consists of an aggregation of three atoms of oxygen, and is

1	2	3	4	1	2	3	4
		Atomic Weights.				Atomic Weights.	
Name.	Atomic Symbols.	Approximate Values.	International Atomic Weights. O=16.00. H=1.008.	**Name.**	Atomic Symbols.	Approximate Values.	International Atomic Weights. O=16.00. H=1.008.
Aluminium	Al	**27**	27.1	*Neodymium*	Nd	**143·6**	143.6
Antimony (*Stibium*)	Sb	**120**	120.2	*Neon*	Ne	**20**	20
Argon	A	**40**	39.9	Nickel	Ni	**59**	58.7
Arsenic	As	**75**	75.0	*Niobium*	Nb	**94**	94
Barium	Ba	**137**	137.4	Nitrogen	N	**14**	14.04
Beryllium (Glucinum)	Be	**9**	9.1	*Osmium*	Os	**191**	191
Bismuth	Bi	**208**	208.5	Oxygen	O	**16**	16.00
Boron	B	**11**	11	Palladium	Pd	**106**	106.5
Bromine	Br	**80**	79.96	Phosphorus	P	**31**	31.0
Cadmium	Cd	**112**	112.4	Platinum	Pt	**195**	194.8
Caesium	Cs	**133**	132.9	Potassium (*Kalium*)	K	**39**	39.15
Calcium	Ca	**40**	40.1				
Carbon	C	**12**	12.00	*Praseodymium*	Pr	**140·5**	140.5
Cerium	Ce	**140**	140.25	*Rhodium*	Rh	**103**	103
Chlorine	Cl	**35·5**	35.45	*Rubidium*	Rb	**85**	85.5
Chromium	Cr	**52**	52.1	*Ruthenium*	Ru	**101·7**	101.7
Cobalt	Co	**59**	59.0	*Samarium*	Sm	**150**	150.3
Copper (*Cuprum*)	Cu	**63·5**	63.6	*Scandium*	Sc	**44**	44.1
Erbium	Er	**166**	166	Selenium	Se	**79**	79.2
Fluorine	F	**19**	19	Silicon	Si	**28**	28.4
Gallium	Ga	**70**	70	Silver (*Argentum*)	Ag	**108**	107.93
Germanium	Ge	**72**	72.5	Sodium (*Natrium*)	Na	**23**	23.05
Gold (*Aurum*)	Au	**197**	197.2	Strontium	Sr	**87·6**	87.6
Helium	He	**4**	4	Sulphur	S	**32**	32.06
Hydrogen	H	**1**	1.008	*Tantalum*	Ta	**183**	183
Indium	In	**115**	115	Tellurium	Te	**125?**	127.6
Iodine	I	**127**	126.97	Thallium	Tl	**204**	204.1
Iridium	Ir	**193**	193	*Thorium*	Th	**232**	232.5
Iron (*Ferrum*)	Fe	**56**	55.9	Tin (*Stannum*)	Sn	**118**	119
Krypton	Kr	**81·5**	81.8	*Titanium*	Ti	**48**	48.1
Lanthanum	La	**138**	138.9	*Tungsten*	W	**184**	184
Lead (*Plumbum*)	Pb	**207**	206.9	*Uranium*	U	**238·5**	238.5
Lithium	Li	**7**	7.03	*Vanadium*	V	**51·2**	51.2
Magnesium	Mg	**24**	24.36	*Xenon*	X	**128**	128
Manganese	Mn	**55**	55.0	*Ytterbium*	Yb	**173**	173
Mercury (*Hydrargyrum*)	Hg	**200**	200	*Yttrium*	Y	**89**	89
				Zinc	Zn	**65**	65.4
Molybdenum	Mo	**96**	96	*Zirconium*	Zr	**90·7**	90.6

represented by the symbol O_3, while the tetr-atomic character of the phosphorus molecule is expressed in the symbol P_4. The composition of compound molecules is expressed by placing the symbols of the atoms which compose such molecules in juxtaposition : thus a molecule consisting of one atom of sodium (symbol Na) and one atom of chlorine (symbol Cl) is represented by the united symbols of these two elements, $NaCl$; a compound consisting of one atom of carbon and one atom of oxygen by the symbols of these two atoms, CO. Such arrangements of symbols representing molecules are termed *molecular formulæ*, or, simply, *formulæ*.

When the molecule contains more than one atom of any particular element, this fact is indicated by the use of numerals placed immediately after the symbol to be multiplied : thus, a molecule of water consists of two atoms of hydrogen and one atom of oxygen, the *formula* for water is therefore H_2O. One molecule of ammonia, consisting of an atom of nitrogen with three atoms of hydrogen, is represented by the formula NH_3; and a molecule of sulphuric acid, which is an aggregation of two atoms of hydrogen, one atom of sulphur, and four atoms of oxygen, has the formula H_2SO_4.

It is sometimes necessary to represent the presence in a molecule of certain groups of atoms, groups which seem to hold together and often to function as a single atom. This is accomplished by the use of brackets : thus $(NH_4)_2SO_4$ is the formula for a molecule containing one atom of sulphur, four atoms of oxygen, eight atoms of hydrogen, and two atoms of nitrogen ; the nitrogen and hydrogen atoms being present as two groups, in each of which one nitrogen atom is associated with four hydrogen atoms. Such groups of atoms are termed *compound radicals*.

When it is required to indicate more than one molecule of the same substance, numerals are placed immediately in front of the formula : thus $2H_2O$ signifies two molecules of water, and $3NH_3$ expresses three molecules of ammonia.

By means of these symbols and formulæ, chemists are enabled to represent, in a concise manner, the various chemical changes which it is the province of chemistry to examine. Such changes are usually termed *chemical reactions*, and they are represented in the form of equations in which the symbols and formulæ of the reacting substances as they are before the change are placed on the left, and those of the substances which result from the change upon the right, thus—

$$H_2 + Cl_2 = 2HCl$$

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

The sign + has a different significance as used on the left side of the equation to that which it bears upon the right. On the left hand it implies that chemical action takes place between the substances, while on the opposite side it has the simple algebraic meaning. Thus, the second of the above equations is understood to mean, that when the compounds, mercuric chloride and potassium iodide, are brought together in such a way that chemical action results, a redistribution of the atoms will take place, resulting in the formation of mercury iodide and also potassium chloride.

As further illustrations of the use of chemical symbols, the following three examples may be given as exemplifying the three modes of chemical action mentioned on page 13 :—

(1) $NH_3 + HCl = NH_4Cl.$

Ammonia combines with hydrochloric acid, and gives ammonium chloride.

(2) $H_2SO_4 + Na_2CO_3 = Na_2SO_4 + CO_2 + H_2O.$

Sulphuric acid combines with normal sodium carbonate, and gives normal sodium sulphate, carbon dioxide, and water.

(3) $(CN)O(NH_4) = (NH_2)_2CO.$

Ammonium cyanate is converted into urea.

In all cases where the nature of the chemical change is understood, it is capable of expression by such equations, and as matter is indestructible, every atom present in the interacting molecules upon the left of the expression reappears on the right-hand side in some fresh association of atoms.*

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* See also Chemical Notation, chapter vii.

CHAPTER V

THE ATOMIC THEORY

THE atomic view as to the constitution of matter, briefly sketched out in Chapter I., forms a part of what is to-day known as the *atomic theory.*

When chemical changes were carefully studied from a *quantitative* standpoint, four laws were discovered in obedience to which chemical action takes place. These laws are distinguished as the laws of chemical combination. Three of these generalisations refer to quantitative relations as respects *weight;* while one expresses quantitative relations with regard to *volume*, and only relates to matter in the gaseous state.

I. Law of Constant Proportion.—*The same compound always contains the same elements combined together in the same proportion by weight;* or expressed in other words, *The weights of the constituent elements of every compound bear an unalterable ratio to each other, and to the weight of the compound formed.*

II. Law of Multiple Proportions.—*When the same two elements combine together to form more than one compound, the different weights of one of the elements which unite with a constant weight of the other bear a simple ratio to one another;* or this law may be stated thus: *When one element unites with another in two or more different proportions by weight, these proportions are simple multiples of a common factor.*

III. Law of Reciprocal Proportions, or **Law of Equivalent Proportions.**--*The weights of different elements which combine separately with one and the same weight of another element, are either the same as, or are simple multiples of, the weights of these different elements which combine with each other;* or in other words, *The relative proportions by weight in which the elements, A, B, C, D, &c., combine with a constant weight of another element, X, are the same for their combinations with any other element, Y.*

IV. Law of Gaseous Volumes, or The Law of Gay-Lussac. —*When chemical action takes place between gases, either elements or compounds, the volume of the gaseous product bears a simple relation to the volumes of the reacting gases.*

These four laws are the foundations upon which the whole superstructure of modern chemistry rests.

(1.) **The Law of Constant Proportions.**—When two substances are mingled together, and remain as a mere mechanical mixture, they may obviously be present in any proportion, and it was at one time thought that when two substances entered into chemical combination with each other, they could do so also in any proportion, and that the composition of the resulting compound would vary from this cause. This belief was finally disproved, and the law of constant proportions definitely established by Proust in the year 1806. The same compound, therefore, however made, and from whatever source obtained, is always found to contain the same elements united together in the same proportion by weight. Thus, common salt, or, to adopt its systematic name, sodium chloride, which is a compound of the two elements sodium and chlorine, may be made by bringing the metal sodium into contact with chlorine gas, when the two elements unite and form this compound. It can also be made by the action of hydrochloric acid upon the metal sodium, or by adding hydrochloric acid to sodium carbonate, and by a variety of other chemical reactions. When the sodium chloride obtained by any or all of these processes is analysed, it is invariably found to contain the elements chlorine and sodium in the proportion by weight of 1 : 0.6479, or, expressed centesimally—

Sodium . .	39.32
Chlorine . .	60.68
	100.00

and when this is compared with the sodium chloride as found in nature, obtained either from the salt-mines of Cheshire, or the celebrated mines in Galicia, or by evaporating sea-water, it is found that the composition of the compound in all cases is exactly the same. In the same way the compound water, consisting of the two elements hydrogen and oxygen, whether it be prepared synthetically by causing the two elements to unite directly, or obtained from any natural source, as rain, or spring, or river, is found to contain its constituent elements hydrogen and oxygen in the ratio by weight of 1 : 8, or,

Hydrogen . .	11.12
Oxygen . .	88.88
	100.00

If in the formation of sodium chloride by the direct combination of its constituent elements, an excess of either one or other be present beyond the proportions 39.32 per cent. of sodium and 60.68 per cent. of chlorine, that excess will simply remain unacted upon. If eight parts by weight of hydrogen and eight parts by weight of oxygen be brought together under conditions that will cause chemical action, the eight parts of oxygen will unite with one part of hydrogen, and the other seven parts of hydrogen merely remain unchanged. This fact, that elements are only capable of uniting with each other in certain definite proportions, marks one of the most characteristic differences between chemical affinity and those other forces, such as gravitation, that are usually distinguished as physical forces; for although there are many instances known in which the *extent* to which a chemical action may proceed (that is, the particular proportion of the reacting bodies which will undergo the permutation that results in the formation of different molecules) is influenced by the *mass* of the acting substances, it never governs the proportion in which the elements combine in these compounds.

It follows from the law of constant composition that the sum of the weights of the products of a chemical action will be equal to that of the interacting bodies; and upon the validity of this law depend all processes of quantitative analyses.

(2.) **The Law of Multiple Proportions** was first recognised by Dalton, who investigated certain cases where the same two elements combine together in different proportions, giving rise to as many totally distinct compounds. These proportions, however, were always found to be constant for each compound so produced, so that this law formed no contradiction to the law of constant composition. The simple numerical relation existing between the numbers representing the composition of such compounds will be evident from the following examples. The two* compounds of

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* In Dalton's day these two substances were the only known compounds of carbon with hydrogen.

carbon with hydrogen, known as *marsh gas* and *ethylene*, are found to contain these elements in the proportions—

Marsh gas . .	1	part by weight of hydrogen with	3	parts of carbon.
Ethylene . .	1	,, ,, ,,	6	,, ,,

The two compounds of carbon with oxygen contain these elements in the proportion—

Carbon monoxide .	1	part of carbon with	1.334	parts of oxygen by weight.
Carbon dioxide .	1	,, ,,	2.667	,, ,, ,,

The elements nitrogen and oxygen form as many as five different compounds, in which the two elements are present in the proportions—

Nitrous oxide . .	1	part of nitrogen with	0.571	parts of oxygen by weight.
Nitric oxide. . .	1	,, ,,	1.143	,, ,, ,,
Nitrogen trioxide .	1	,, ,,	1.714	,, ,, ,,
Nitrogen peroxide	1	,, ,,	2.286	,, ,, ,,
Nitrogen pentoxide	1	,, ,,	2.857	,, ,, ,,

The relative proportions of carbon combining with a constant weight of hydrogen in the two first compounds are as 1 : 2.

Those of oxygen uniting with a constant weight of carbon in the second example are also as 1 : 2, while in the nitrogen series the relative proportions of oxygen in combination with a constant weight of nitrogen are as 1 : 2 : 3 : 4 : 5.

(3.) **Law of Reciprocal Proportions.**—Known also as the law of proportionality, or the law of equivalent proportions. When the weights of various elements, which were capable of uniting separately with a given mass of another element, were compared together, it was seen that these weights bore a simple relation to the proportions in which these elements combined amongst themselves. For example, the elements chlorine and hydrogen each separately combine with the same weight of phosphorus, the proportions being—

Phosphorus : chlorine = 1 : 3.43
Phosphorus : hydrogen = 1 : 0.097

The elements chlorine and hydrogen can combine together, and they do so in the proportion—

Chlorine : hydrogen = 35.5 : 1
but 35 : 1 = 3.43 : 0.097

Therefore the proportions by weight in which chlorine and hydrogen separately combine with phosphorus is a measure of the proportion in which they will unite together.

Again, the two elements carbon and sulphur each separately combine with the same weight of oxygen, the proportion being—

Oxygen : carbon = 1 : 0.375
Oxygen : sulphur = 1 : 1

But the elements carbon and sulphur themselves unite together, and in the proportion—

Carbon : sulphur = 0.1875 : 1
but 0.1875 : 1 = 0.375 : 2

Therefore the proportion by weight in which carbon and sulphur separately unite with the same mass of oxygen is a *simple multiple* of that in which these two elements combine together. These remarkable numerical relations will be rendered still more evident by comparing the proportions in which the members of a series of elements combine with a constant weight of various other elements: thus—

Hydrogen.	Sodium.	Potassium.	Silver.	Mercury.	Chlorine.
0.02817	0.6479	1.02	3.04	2.816	unite separately with 1 part.

It will be seen that the proportion in which these numbers stand to each other is as—

1 : 23 : 39 : 107 : 100 : 35.5

Let us now compare these proportions with those in which the same elements unite with a constant weight of the element bromine—

Hydrogen.	Sodium.	Potassium.	Silver.	Mercury.	Bromine.
0.0125	0.2875	0.4875	1.34	1.25	unite with 1 part,

or as—

1 : 23 : 39 : 107 : 100 : 80

Each of these five elements in like manner combines with oxygen, and the weights which are found to unite with a constant mass of oxygen are—

Hydrogen.	Sodium.	Potassium.	Silver.	Mercury.	Oxygen.
0.125	2.875	4.875	13.38	12.5	unite with 1 part,

again as—

1 : 23 : 39 : 107 : 100 : 8

The same relation will appear in the case of the combination of these five elements with a constant weight of sulphur—

Hydrogen.	Sodium.	Potassium.	Silver.	Mercury.	Sulphur.
0.0625	1.4375	2.4375	6.69	6.25	unite with 1 part.

or as—

1 : 23 : 39 : 107 : 100 : 16

It is thus evident that the proportions in which the members of such a series combine with a constant weight of one element is the same as that in which they unite with a constant mass of another element. One part by weight of hydrogen combines with 35.5 parts of chlorine, 80 parts of bromine, 8 parts of oxygen, and 16 parts of sulphur—that is to say, these proportions of these four elements satisfy the chemical affinity of 1 part of hydrogen ; they are therefore said to be *equivalent.* Twenty-three parts of sodium is likewise equivalent to 35.5 parts of chlorine, 80 parts of bromine, 8 parts of oxygen, and 16 parts of sulphur, and by the same reasoning it is also equivalent to 1 part of hydrogen, 39 parts of potassium, 107 parts of silver, and 100 parts of mercury. These numbers, therefore, are known as the *equivalent weights* of the elements, or their *combining proportions*, and the combining weight of an element may therefore be defined as the smallest weight of that element which will combine with 1 part by weight of hydrogen.

This law of proportionality, or reciprocal proportion, was discovered by Richter, but it was left for Dalton to trace the connection between these three generalisations. Dalton adopted and adapted an ancient theory concerning the ultimate constitution of matter which was expounded by certain of the early Greek philosophers. The exponents of this theory held that matter is built up of vast numbers of minute indivisible particles, in opposition to the antagonistic theory believed by others, namely, that matter was absolutely homogeneous and capable of infinite subdivision.

Dalton embraced the ancient doctrine of atoms, and extended it into the scientific theory which is to-day known as Dalton's atomic theory, and is accepted as a fundamental creed by modern chemists.

According to this theory, matter consists of aggregations of minute particles, or atoms, which are indivisible. Dalton conceived that chemical combination takes place between atoms—that is to say, when chemical action takes place between two elements, it is due to the union of their atoms ; the atoms, coming into juxtaposition with each other under the influence of chemical affinity, are held together by the operation of this force. He further assumed that the atoms of the various elements possessed different relative weights, and that the relations existing between these weights was the same as that between the weights in which experiment had shown the elements to be capable of combining together. In other words, he said that the numbers representing the *combining proportion* of the elements expressed also the relative weights of the atoms.

Let us now see how this theory satisfies and explains the first three laws of chemical combination.

(1.) **The Law of Constant Composition.**—It has already been shown (p. 26) that the compound sodium chloride, wheresoever and howsoever obtained, contains the elements chlorine and sodium in the proportion—

Chlorine : sodium = 1 : 0.6479.

These numbers have been shown on p. 29 to represent the combining proportions—

Chlorine : sodium = 35.5 : 23.

Now the atomic theory states, that sodium chloride is formed by the union of *atoms* of chlorine with *atoms* of sodium, and that the relative weights of these atoms is expressed by the combining weights of the elements, namely, 35.5 and 23. If therefore, sodium is to combine with chlorine, since atoms are indivisible masses, it follows that the compound produced by the union of one atom of each of these two elements must always have the same composition.

(2.) **The Law of Multiple Proportions.**—The ratio in which oxygen combines with hydrogen to form the compound water is seen on p. 27 to be as 8 : 1. This number 8, therefore, we will for the present argument regard as the relative weight of the atom of oxygen.*

Oxygen combines with carbon as already mentioned, forming two different compounds ; in the first, the elements are present in the proportion—

Carbon : oxygen = 1 : 1.334 = 6 : 8,

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* For reasons which will be explained later, chemists now regard the number 16 as representing (in round numbers) the relative weight of the atom of oxygen.

that is to say, in the proportion of one atom of carbon to one atom of oxygen. According to the theory, if the atom of carbon unites with more oxygen than *one* atom, it must at least be with *two* atoms. It may be with three or with four, but as the compound must be formed by the accretion of these indivisible atoms, the increment of oxygen must take place by multiples of 8. When the second compound is examined it is found to contain its constituent elements in the proportion—

Carbon : oxygen = 1 : 2.667 = 6 : 16,

that is to say, in the proportion of one atom of carbon to two atoms of oxygen. This information respecting the composition of these two compounds is conveyed both in their names and their formulæ. The first is termed carbon *mon*oxide, and its formula is expressed by the symbol CO ; while the second is distinguished as carbon *di*oxide, and has the formula CO_2.

The difference in the composition of the five compounds that nitrogen forms by union with oxygen will be made evident by the aid of this theory. The proportion of nitrogen to oxygen in these compounds is—

(1.) Nitrogen : oxygen = 1 : 0.571 = 14 : 8
(2.) Nitrogen : oxygen = 1 : 1.143 = 14 : 16
(3.) Nitrogen : oxygen = 1 : 1.714 = 14 : 24
(4.) Nitrogen : oxygen = 1 : 2.268 = 14 : 32
(5.) Nitrogen : oxygen = 1 : 2.857 = 14 : 40

And it will be seen that the increase in the proportion of oxygen in the compounds takes place by the regular addition of a weight of that element equal to 8, which at the present stage of the argument we are regarding as representing the relative weight of the atom of oxygen.

(3.) **The Law of Reciprocal Proportions.**—If the illustrations given on p. 28 of the operation of this law be examined in the light of the atomic theory, their explanation will be evident : thus, the relative proportions in which hydrogen and chlorine separately combine with phosphorus is 0.097 : 3.43, and the ratio between these numbers is as 1 : 35.5, which is the proportion in which these two elements are known to unite together to form hydrochloric acid. These numbers, however, represent the relative weights of the *atoms* of these elements, therefore hydrochloric acid may be supposed to be formed by the union of one atom of hydrogen with one atom of chlorine.

Again, the relative weights of carbon and sulphur which separately combine with a constant weight of oxygen are—carbon, 0.375; sulphur, 1; and the ratio between these numbers is as 6 : 16.

Carbon and sulphur, however, unite together in the relative proportion—

Carbon : sulphur = 0.1875 : 1 = 6 : 32.

Therefore the compound they produce may be supposed to consist of one atom of carbon, having the relative weight 6, and *two* atoms of sulphur, each with the relative weight 16.

CHAPTER VI

ATOMIC WEIGHTS

In the third column of the table on page 22, the numbers are given which are at the present time generally accepted by chemists as representing the approximate atomic weights of the elements. These numbers depart, in many instances, from those arrived at by Dalton's methods : thus, the relative weights of carbon, oxygen, nitrogen, and sulphur, which were found to be equivalent to one part of hydrogen, are—carbon = 6,* oxygen = 8, nitrogen = 4.66, sulphur = 16 ; while the figures given as the approximate atomic weights of these elements in the table are—carbon = 12, oxygen = 16, nitrogen = 14, sulphur = 32. We must now discuss some of the chief reasons for these departures. In the two compounds of carbon and hydrogen known to Dalton, namely, marsh gas and ethylene, the proportions of carbon to hydrogen are—

In ethylene . . . Carbon : hydrogen = 6 : 1.
In marsh gas . . Carbon : hydrogen = 6 : 2.

Dalton therefore concluded that ethylene was a compound containing 1 atom of carbon united with 1 atom of hydrogen, and to which, therefore, he gave the formula CH ; and that marsh gas consisted of 1 atom of carbon combined with 2 atoms of hydrogen, and which he accordingly represented by the formula CH_2.

There was, however, nothing to prove that the weight of *carbon* was constant in the two compounds, for it will be obvious that the same ratio between the weight of carbon and hydrogen will still be maintained by assuming that the *hydrogen* is constant, and that the carbon varies, thus—

In marsh gas . . Hydrogen : carbon : : 1 : 3.
In ethylene . . Hydrogen : carbon : : 1 : 3×2.

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* These are the numbers which Dalton ought to have obtained had his methods of determination been more exact. The figures he actually found for the combining weights of these four elements were respectively, 5, 7, 5, 13.

That is to say, the ratios are not disturbed by the assumption that in marsh gas we have 1 atom of hydrogen combined with 1 atom of carbon, having the relative combining weight of 3, and in ethylene 1 atom of hydrogen united with 2 atoms of carbon.

It will be evident, however, that if we could gain any exact information as to the actual number of atoms which are present in these various molecules, this difficulty would no longer exist.

For example, suppose it were possible to ascertain that in the molecule of marsh gas there were 4 atoms of hydrogen, then as the relative weights of hydrogen and carbon in this compound are as 1 : 3, the weight of the carbon atom would obviously have to be raised from 3 to 12; and if it could be determined that in the ethylene molecule there were also 4 atoms of hydrogen, then seeing that the ratio of hydrogen to carbon in this substance is as 1 : 6, we should conclude that it contained 2 atoms of carbon, of the relative weight not less than 12, and the composition of the two compounds would be expressed by the formulæ, marsh gas CH_4, ethylene C_2H_4.

Again, the relative weights of hydrogen and oxygen in water are as 1 : 8. If the molecule of water contains only 1 atom of hydrogen, then we conclude that 8 represents the relative weight of the oxygen atom, and the formula for water will be HO. But suppose it to be discovered that there are two atoms of hydrogen in a molecule of this compound, then it becomes necessary, in order to retain the ratio between the weight of these constituents (a ratio ascertained by analysis), to double the number assigned to the oxygen atom and to regard its weight as 16, as compared with 1 atom of hydrogen, and the formula for water in this case would be H_2O.

The compound ammonia contains the elements hydrogen and nitrogen in the ratio—

Hydrogen : nitrogen : : 1 : 4.66.

If the molecule of ammonia contains only 1 atom of hydrogen, then 4.66 represents the relative weight of the nitrogen atom, and the formula will be NH; but if it should be found that there are 3 atoms of hydrogen in this molecule, then again the relative weight assigned to the nitrogen must be trebled in order to preserve the ratio, and it will have to be raised from 4.66 to 14 (in round numbers), and the formula for ammonia will be NH_3.

From these considerations it will be evident, that it is of the highest importance to gain accurate knowledge as to the actual number of atoms which are contained in the molecules of matter—in other words, to learn the true atomic composition and structure of molecules; and it may be said that this problem has occupied the minds of chemists from the time that Dalton published his atomic weights, in the year 1808, down to the present time. There is no single method of general application, by means of which chemists are able to determine the atomic weight of an element; but they are guided by a number of independent considerations, some of which are chemical in their character, while others are of a physical nature; and that particular number which is in accord with the most of these considerations, or with what are judged to be the most important of them, is accepted as the true atomic weight.

The chief methods employed for determining atomic weights may be arranged under the following four heads:—

1. Purely chemical methods.
2. Methods based upon volumetric relations.
3. Methods based upon the specific heats of the elements.
4. Method based upon the isomorphism of compounds.

1. As an illustration of the chemical processes from which atomic weights may be deduced, the following examples may be given, namely, the case of the two elements oxygen and carbon.

Oxygen combines, as already stated, with hydrogen in the proportion—

$$\text{Hydrogen} : \text{oxygen} = 1 : 8.$$

When water is acted upon by the element sodium, the compound is decomposed and hydrogen is evolved; and it is found that if 18 grammes of water are so acted on, 1 gramme of hydrogen is evolved, and 40 grammes of a compound are formed, which contains sodium, together with all the oxygen originally in the 18 grammes of water, and some hydrogen. This compound, under suitable conditions, can be acted upon by metallic zinc, and when these 40 grammes are so acted on, 1 gramme of hydrogen is again evolved, and 72.5 grammes are obtained of a compound containing no hydrogen, but sodium and zinc combined with all the oxygen originally contained in the 18 grammes of water.

It will be evident, therefore, that the hydrogen contained in water can be expelled in two equal moieties; there must, therefore, be *two* atoms of hydrogen in this compound. By no known process can the *oxygen* be withdrawn from water in two stages: thus, if 18 grammes of water are acted upon by chlorine, under the conditions in which chemical action can take place, 73 grammes of a compound containing only chlorine and hydrogen are formed, and the whole of the oxygen is thrown out of combination and evolved as gas. It is therefore concluded that water contains in its molecule 2 atoms of hydrogen and 1 atom of oxygen, and as they are combined in the relative proportion of 1 : 8, the atomic weight of oxygen cannot be less than 16.

No compounds have been found in which a smaller weight of oxygen, relative to one atom of hydrogen, than is represented by the number 16 (approximately), is known to take part in a chemical change.

The compound *marsh gas* contains hydrogen and carbon in the proportion by weight of 1 : 3. By acting on this compound with chlorine, it is possible to remove the hydrogen from it in four separate portions.

By the first action of chlorine upon 16 grammes of marsh gas, 1 gramme of hydrogen is removed in combination with 35.5 grammes of chlorine, and a compound containing carbon, hydrogen, and chlorine, in the ratio 12 : 3 : 35.5, is formed.

By the successive action of chlorine, three other moieties of hydrogen can be thus withdrawn, each being in combination with its equivalent (35.5 parts) of chlorine. The second and third compounds that are formed contain carbon, hydrogen, and chlorine in the ratios $12 : 2 : (35.5 \times 2)$ and $12 : 1 : (35.5 \times 3)$.

The compound produced by the fourth action of chlorine, which withdraws the fourth portion of hydrogen, contains only carbon and chlorine, in the ratio $12 : (35.5 \times 4)$. From the fact that the hydrogen contained in marsh gas can thus be removed in four separate portions, the molecule must contain four hydrogen atoms, and therefore the atomic weight of carbon must be at least 12. No compounds of carbon are known in which a smaller weight of carbon, relative to one atom of hydrogen, than is represented by the number 12, takes part in a chemical change.

The definition of atomic weight, furnished by considerations of a chemical nature, may be thus stated: the atomic weight of an element, is the number which represents how many times heavier the smallest mass of that element capable of taking part in a chemical change is, than the smallest weight of hydrogen which can so function.

The choice of hydrogen as the unit of atomic weights is a purely arbitrary selection; but since atomic weight values can only be determined *relatively*, it becomes necessary to select some one element and to assign to its atom some particular number to serve as a standard. As hydrogen is the lightest of all elements, Dalton originally adopted it, and arbitrarily fixed unity as the number which should stand for its atomic weight. The disadvantages of this particular unit are twofold: in the first place the number of elements that form hydrogen compounds that are suitable for atomic weight determinations is very small, whereas nearly all the elements form convenient oxygen compounds, or compounds with elements whose atomic weights with reference to oxygen are accurately known, and in actual practice such compounds are almost always made use of for such determinations. In the second place, the *exact* ratio of the weights of an atom of hydrogen and oxygen is not known with certainty, so that in calculating atomic weights that are determined with reference to oxygen, possible errors may arise. The ratio Hydrogen : Oxygen is *not* exactly 1 : 16. Various values have been obtained by different experimenters, and at the present time 1 : 15.88 is accepted as more nearly the truth.

On account of the extreme difficulty of exactly determining this ratio, chemists are now generally agreed in adopting as the unit in all exact determinations of atomic weights a number which is $\frac{1}{16}$th the weight of the atom of oxygen: that is to say, the atomic weight of oxygen is in reality the standard, and is fixed as 16, and the unit, instead of being the weight of one atom of hydrogen, is $\frac{1}{16}$th of this number.

The effect of this change is only of importance in cases of chemical investigation where a high degree of exactitude is required; for purposes of ordinary analyses and chemical calculations the difference that it makes is practically *nil.* Fixing the atomic weight of oxygen at 16 merely raises the atomic weight of hydrogen from 1 to 1.008. As the use of small decimal fractions introduces unnecessary complications which tend to obscure simple processes of reasoning, the approximate atomic weights given in the third column of page 22 will be employed for the most part in the following Introductory chapters.

The student will frequently meet with slight discrepancies between the numbers given as the atomic weights of various elements by different writers. Such discrepancies are often due to the fact that in some cases $H = 1$ is used as the standard, and in others $O = 16$. For example, the atomic weight of gold will be 195.7 in the first case, and 197.2 in the second; while with the lighter metal aluminium the numbers will be 26.9 as against 27.1.

The discrepancy may also arise from the fact that the determination of atomic weights by different experimenters often vary very considerably. With a view to arrive at some uniformity, a conference of representative chemists was held to consider the subject, and the atomic weights finally decided upon by them were published under the title of *International Atomic Weights.* A revised list of these weights is published annually in the *Berichte*, and in the fourth column of the table on p. 22 will be found the latest values (1905).

2. **Determination of Atomic Weights from Considerations based upon Volumetric Relations. The Law of Gaseous Volumes.**—In the year 1805 the fact was discovered by Gay-Lussac and Humboldt, that when 1 litre of oxygen combines with

2 litres of hydrogen the vapour of water (or steam) which was produced occupied 2 litres, the volumes in all cases being measured under the same conditions of temperature and pressure.* This fact led to the discovery of the simple relation existing between the volumes of other reacting gases and the volume of the products: thus it was found that—

1 vol. of hydrogen unites with 1 vol. of chlorine, and gives 2 vols. of hydrochloric acid.
1 vol. of hydrogen unites with 1 vol. of bromine vapour, and gives 2 vols. of hydrobromic acid.
2 vols. of hydrogen unite with 1 vol. of oxygen, and give 2 vols. of steam.
2 vols. of carbon monoxide unite with 1 vol. of oxygen, and give 2 vols. of carbon dioxide.
1 vol. of carbon monoxide unites with 1 vol. of chlorine, and gives 1 vol. of phosgene gas.

In the same way with compounds that cannot be obtained by the direct union of their constituent elements, it is found that on being subjected to processes of decomposition similar simple volumetric relations exist: thus by suitable methods of decomposition—

2 vols. of ammonia gas yield 1 vol. of nitrogen and 3 vols. of hydrogen.
2 vols. of nitrous oxide yield 2 vols. of nitrogen and 1 vol. of oxygen.
2 vols. of nitric oxide yield 1 vol. of nitrogen and 1 vol. of oxygen.
1 vol. of marsh gas yields 2 vols. of hydrogen and some solid carbon, which cannot be volatilised, and therefore its vapour volume is unknown.
1 vol. of ethylene yields 2 vols. of hydrogen and solid carbon as in the preceding.

The observations of these and similar facts gave rise to the law of Gay-Lussac, and it will be seen that there is evidently a close connection between the simple *volumetric* relations and those existing between the multiple proportions by *weight*, in which one

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* For the relations of gaseous volumes to temperature and pressure the student is referred to chapter ix., on the general properties of gases.

element unites with another. For example, in the two oxides of nitrogen the ratios of the two elements by weight are—

Nitrous oxide . . . Nitrogen : oxygen = 28 : 16.
Nitric oxide . . . Nitrogen : oxygen = 14 : 16,

while the volumetric relation in which the two constituents are present is—

Nitrous oxide . . . Nitrogen : oxygen = 2 : 1.
Nitric oxide . . . Nitrogen : oxygen = 1 : 1.

In other words, there is twice as much nitrogen by *weight* in the one compound as in the other, and there is twice as much nitrogen by *volume* in the one as compared to the other. Moreover, if 14 and 16 respectively represent the relative weights of atoms of nitrogen and oxygen, then the numbers representing the relative *volumes* in which these elements unite will also express the number of atoms of each in the molecule.

The connection existing between the proportions in which elements unite by weight, and by volume, was first explained by the Italian physicist and chemist Avogadro, who in the year 1811 advanced the theory now recognised as a fundamental principle, and known as Avogadro's hypothesis. This theory may be thus stated: *Equal volumes of all gases or vapours, under the same conditions of temperature and pressure, contain an equal number of molecules.* If this be true, if there are the same *number* of molecules in equal volumes of all gases, it must follow that the ratio between the weights of equal volumes of any two gases will be the same as that between the single molecules of the particular gases. If a litre of oxygen be found to weigh sixteen times as much as a litre of hydrogen (under like conditions of temperature and pressure), inasmuch as there are the same number of molecules in each, the oxygen molecule must be sixteen times heavier than that of hydrogen; and therefore by the comparatively simple method of weighing equal volumes of different gases, it becomes possible to arrive at the relative weights of their molecules.

The relative weights of equal volumes of gases and vapours, in terms of a given unit, are known as their *densities* or *specific gravities.* Sometimes densities are referred to air as the unit, but more often hydrogen, as being the lightest gas, is taken as the standard. Taking hydrogen as the unit, the density or specific gravity of a gas is the weight of a given volume of it, as compared with the weight of the same volume of hydrogen—or in other words, the ratio between the weight of a molecule of that gas and a molecule of hydrogen. The ratio that exists between the weight of a gaseous molecule and *half the weight of a molecule of hydrogen*, chemists term the *molecular weight* of that gas; hence it will be obvious that the number which represents the molecular weight of a gas is double that of its density or specific gravity.

If 1 litre of hydrogen and 1 litre of chlorine be caused to combine, 2 litres of gaseous hydrochloric acid are formed. As equal volumes of all gases (under like conditions) contain the same number of molecules, in the 2 litres of hydrochloric acid there must be twice as many molecules of that compound as there were of hydrogen molecules in the 1 litre, or of chlorine molecules in the other. But each molecule of hydrochloric acid is composed of chlorine and hydrogen (from other considerations one atom of each element), therefore there must have been at least twice as many atoms of hydrogen in the litre of that gas as there were molecules; and by the same reasoning, twice as many chlorine atoms in the litre of chlorine as there were molecules: in other words, both hydrogen and chlorine molecules consist of *two* atoms. The molecular weight of hydrogen therefore is 2; that is, its molecule is twice as heavy as its atom. The *atom* of hydrogen is the unit to which molecular weights are referred, while the weight of the molecule of hydrogen is taken as the standard of densities or specific gravities.

In order, therefore, to find the molecular weight of any gas or vapour, it is necessary to learn its density—that is, to ascertain how many times a given volume of it is heavier than the same volume of hydrogen,* and to double the number so obtained.†

The following table gives the densities or specific gravities of all the elements whose vapour densities have been determined. The list includes all those elements which are gases at the ordinary temperature, and those that can be vaporised under conditions

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* Certain exceptions to this rule are discussed under the subject of Dissociation, chap. x. p. 88.

† The specific gravity of hydrogen, as compared with air taken as unity, is 0.0695, or air is 14.3875 times heavier than hydrogen. If, therefore, it be desired to find the molecular weight of a given gas, whose density as compared with air is known, it is only necessary to multiply its density (air = 1) by the number 14.3875, which gives its density as compared with hydrogen, and then to double the number so obtained.

which render such determinations experimentally possible. (Hydrogen being taken as unity, the other numbers are the approximate values, which for purposes of discussion are more suitable than figures that run to two or three decimal places.)

Hydrogen	1	Selenium	79
Helium	2	Bromine	80
Neon	10	Iodine	127
Nitrogen	14	Sodium	11.5
Oxygen	16	Potassium	19.5
Fluorine	19	Zinc	32.5
Argon	20	Cadmium	56
Sulphur	32	Mercury	100
Chlorine	35.5	Phosphorus	62
Krypton	41	Arsenic	150
Xenon	64.0		

Let us now consider how the knowledge of the relative weights of gaseous molecules is utilised in assigning a particular number as the atomic weight of an element.

The molecular weight of chlorine is 71. It has been shown that the molecule certainly contains more than 1 atom, and *probably* 2, in which case 35.5 would represent the relative weight of the atom.

The compound hydrochloric acid has the molecular weight 36.5. It has been already proved that this compound contains 1 atom of hydrogen, therefore $36.5 - 1 = 35.5$.

The compound carbon tetrachloride gives a molecular weight 154. Analysis shows that this compound contains 12 parts of carbon in 154 parts, therefore $154 - 12 = 142 = 35.5 \times 4$.

In these three molecules the weights of chlorine relative to the weight of 1 atom of hydrogen are 142, 35.5, and 71, the greatest common divisor of which is 35.5. This number, therefore, is selected as the atomic weight of chlorine.

Again, it has been shown that by the action of metals upon water, the hydrogen contained in the water could be expelled in two separate portions, thus proving that there must be 2 atoms of hydrogen in the molecule of that compound.

The molecular weight of water is found to be 18; deducting from this the weight of the two hydrogen atoms we get $18 - 2 = 16$.

The molecular weight of carbon monoxide is 28; 28 parts of this compound contain 12 parts of carbon, therefore $28 - 12 = 16$.

The molecular weight of carbon dioxide is 44; 44 parts of this compound also contain 12 parts of carbon, therefore $44-12=32$.

When 1 litre of oxygen combines with two litres of hydrogen, 2 litres of water vapour are formed; there are therefore twice the number of water molecules produced as there are oxygen molecules (since by Avogadro's hypothesis 2 litres contain twice as many molecules as 1 litre). But each water molecule contains certainly 1 atom of oxygen, therefore the original oxygen molecules must have consisted of not less than 2 atoms. When the density of oxygen is determined it is found to be 16, its molecular weight therefore is 32.

In these four various molecules the weights of oxygen relative to the weight of 1 atom of hydrogen are 16, 16, 32, 32, the greatest common divisor of which is 16. This number, therefore, is selected as the atomic weight of oxygen.

Again, it has already been shown that in the compound ammonia, the hydrogen can be removed in three separate moieties, proving that there must be three atoms of that element in the molecule. The molecular weight of ammonia is found to be 17, therefore $17-3=14$, which is the weight of the nitrogen.

The molecular weight of nitrous oxide is 44; 44 parts of this compound are found to contain 16 parts of oxygen and 28 parts of nitrogen.

The molecular weight of nitric oxide is 30; 30 parts of this compound contain 16 parts of oxygen and 14 parts of nitrogen.

The molecular weight of nitrogen is found to be 28.

In these four different molecules the weights of nitrogen relative to the weight of 1 atom of hydrogen are 14, 28, 14, 28, the greatest common divisor of which is 14. The atomic weight of nitrogen, therefore, is regarded as 14.

These three examples, namely, chlorine, oxygen, and nitrogen are instances of elements which are gaseous at ordinary temperatures; but the same methods are applicable in the case of the non-volatile elements, such as carbon, provided they furnish a number of compounds that are readily volatile.

On comparing the numbers in the foregoing table (p. 42), representing the densities of various elements, with the atomic weights of those elements as given on p. 22, it will be seen that in several cases the numbers given are approximately the same. This agreement is merely because the molecules of these elements consist of two atoms. The molecules of helium, neon, argon, krypton, xenon, sodium, potassium, zinc, cadmium, and mercury consist of only one atom; their atomic weights, therefore, will be the same as their molecular weights, that is, twice their densities. The elements arsenic and phosphorus, on the other hand, contain in their molecules four atoms—that is to say, the number which represents the smallest weight of phosphorus and of arsenic, capable of taking part in a chemical change, is only half the density, and therefore a fourth of the molecular weight.

The definition of atomic weight that is furnished by the consideration of volumetric relations may be thus stated. *The atomic weight is the smallest weight of an element that is ever found in a volume of any gas or vapour equal to the volume occupied by one molecule of hydrogen at the same temperature and pressure.*

The volume occupied by one molecule of hydrogen is regarded as the standard molecular volume, while that occupied by an atom of hydrogen—or, in other words, the atomic volume of hydrogen—is called the *unit volume.* The standard molecular volume, therefore, is said to be *two unit volumes;* and as, from Avogadro's law, all gaseous molecules have the same volume, it follows that the molecules of all gases and vapours occupy two unit volumes. Atomic weight may therefore be defined as *the smallest weight of an element ever found in two unit volumes of any gas or vapour.*

The molecular volume of a gas is its molecular weight divided by its relative density, a ratio which in all cases will obviously equal 2, that is, two unit volumes.

The atomic volume of an element in the state of vapour is its atomic weight divided by its relative density. In the case of such elements as chlorine, nitrogen, oxygen, &c., whose molecules are diatomic, the quotient will be 1—that is to say, the atomic volume of these elements is equal to 1 unit volume. In the case of mercury vapour, however, we have $\frac{\text{atomic weight} = 200}{\text{density} = 100} = 2$.

The atomic volume of mercury vapour, therefore, is equal to 2 unit volumes, and is identical with its molecular volume.

On the other hand, with the element phosphorus the atomic volume is $\frac{\text{atomic weight} = 31}{\text{density} = 62} = .5$, or one-half the unit volume, and therefore one-fourth the molecular volume; consequently, four atoms exist in this molecule.

The method of determining atomic weights based upon volumetric relations, when taken by itself, is not an absolutely certain criterion, for although the atomic weight of an element cannot be *greater* than the smallest mass that enters into the composition of the molecules of any of its known compounds, it might be *less* than this, as there is always the possibility of a new compound being discovered, in which the relative weight of an element is such as to make it necessary to halve the previously accepted atomic weight.

3. **Determination of Atomic Weight from the Specific Heat of Elements in the Solid State.**—When equal weights of different substances are heated through the same range of temperature, it is found that they absorb very different quantities of heat, and on again cooling to the original temperature, they consequently give out different amounts of heat. Thus, if 1 kilogramme of water, and 1 kilogramme of mercury be each heated to a temperature of 100°, and then each be poured into a separate kilogramme of water at 0°, in the first case the resultant mixture will have a temperature of 50°, while in the second it will only reach the temperature of 3.2°; that is to say, while the water in cooling through 50° has raised the temperature of an equal weight of water from 0° to 50°, the amount of heat in 1 kilogramme of mercury at 100° has only raised the temperature of an equal weight of water from 0° to 3.2°, and in so doing has itself become lowered in temperature $100 - 3.2 = 96.8°$. The amount of heat contained, therefore, in equal weights of water and of mercury at the same temperature, as shown by these figures, is as—

$$\frac{50}{50} : \frac{3.2}{96.8} = 1 : \tfrac{1}{30};$$

therefore it requires 30 times as much heat to raise a given weight of water through a given number of degrees as to raise an equal weight of mercury through the same interval of temperature, or the *thermal capacity* of mercury is $\frac{1}{30}$th that of water.

The specific heat of a substance is the ratio of its thermal capacity to that of an equal weight of water; or, the ratio between the amount of heat necessary to raise a unit weight of the substance from 0° to 1°, and that required to raise the same weight of water from 0° to 1°; thus, the specific heat of mercury is $\frac{1}{30}$, or 0.033. Water is chosen as the standard of comparison because it possesses the highest thermal capacity of all known substances; the numbers, therefore, which express the specific heats of other substances are all less than unity.

Dulong and Petit were the first to draw attention (1819) to a remarkable relation which exists between the specific heats and the atomic weights of various solid elements, whose specific heats they themselves had determined. They found that the specific heats of the solid elements were inversely as their atomic weights; that is to say, the capacity for heat of masses of the elements proportional to their atomic weight was equal. This law, known as the law of Dulong and Petit, may be thus stated: *The thermal capacities of atoms of all elements in the solid state are equal.*

The thermal capacity of an atom is termed its *atomic heat;* hence the law may be more briefly stated, *all elements in the solid state have the same atomic heat.* This important constant is the product of the atomic weight into the specific heat. From the following table it will be seen that the number expressing the atomic heat is not perfectly constant: the departures from the mean 6.4 are, as a rule, only slight, and may be attributed to the fact that the determinations are not always made upon the elements under conditions that are strictly comparable. At the end of the table, however, there are certain elements which appear to present marked exceptions to the law.

Element.	Specific Heat.		Atomic Weight.		Atomic Heat.
Lithium	0.94	×	7	=	6.6
Sodium	0.29	×	23	=	6.7
Potassium	0.166	×	39	=	6.5
Manganese	0.122	×	55	=	6.7
Iron	0.112	×	56	=	6.3
Silver	0.057	×	108	=	6.1
Gold	0.032	×	196	=	6.2
Mercury (solid)	0.032	×	200	=	6.4
Lead	0.031	×	206.4	=	6.5
Beryllium	0.41	×	9.1	=	3.7
Boron (cryst.)	0.25	×	11	=	2.75
Carbon (diamond)	0.147	×	12	=	1.76
Silicon (cryst.)	0.177	×	28	=	4.95

It will be seen that, relatively speaking, the four elements which show a considerable departure from the law of Dulong are elements with low atomic weights. Low atomic weight, however, is not *always* accompanied by such deviation, as is shown in the case of lithium and sodium.

When the different allotropes of carbon are experimented upon, it is found that the departure is not the same for each modification of the element, thus—

Element.	Specific Heat.		Atomic Weight.		Atomic Heat.
Diamond	0.147	×	12	=	1.76
Graphite	0.200	×	12	=	2.40
Charcoal	0.241	×	12	=	2.90

It has been observed that, as a general rule, the specific heat of an element is slightly higher at higher temperatures ; but in the case of the four elements showing abnormal atomic heats, this increase rises rapidly with increased temperature, until a certain point is reached, when it remains practically constant, and represents an atomic heat which closely approximates to the normal value ; thus in the case of diamond, the specific heat at increasing temperatures is—

	Specific Heat.		Atomic Weight.		Atomic Heat.
Diamond at 10.7°	0.1128	×	12	=	1.35
„ 45°	0.1470	×	12	=	1.76
„ 206°	0.2733	×	12	=	3.28
„ 607°	0.4408	×	12	=	5.30
„ 806°	0.4489	×	12	=	5.4
„ 985°	0.4589	×	12	=	5.5

The same result is seen in the case of graphite, and it is also to be remarked, that while at low temperatures there exists a wide difference between the specific heats of these two modifications of carbon, this difference vanishes at a temperature of about 600°.

	Specific Heat.		Atomic Weight.		Atomic Heat.
Graphite at 10.8°	0.1604	×	12	=	1.93
„ 61.3°	0.1990	×	12	=	2.39
„ 642°	0.4454	×	12	=	5.35
„ 978°	0.4670	×	12	=	5.50

Both the elements boron and silicon are found to follow the same rule, and at moderate temperatures their atomic heats nearly approximate the normal constant.

The case of the somewhat rare element beryllium is of special interest from another point of view, which will be referred to when treating of the natural classification of the elements : from the following numbers* it will be seen that its atomic heat very rapidly rises with moderate increase of temperature.

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* Humpidge.

	Specific Heat.		Atomic Weight.		Atomic Heat.
Beryllium at 100°	0.4702	×	9.1	=	4.28
„ 200°	0.5420	×	9.1	=	4.93
„ 400°	0.6172	×	9.1	=	5.61
„ 500°	0.6206	×	9.1	=	5.65

The relation between atomic weight and specific heat, established by Dulong and Petit, is of service in the determination of atomic weights, not as a method of ascertaining the exact value with any degree of refinement, but rather as a means of deciding between two numbers which are multiples of a common factor.

If specific heat × atomic weight = atomic heat, it will be obvious that, if we experimentally determine the specific heat, and divide that value into the constant atomic heat, 6.4, we obtain the approximate atomic weight.

The two following examples will serve to illustrate the application of the method.

The element indium combines with chlorine in the proportion—

Indium : chlorine = 37.8 : 35.5.

If InCl is the formula, then 37.8 is the atomic weight of indium; but from the chemical similarity between indium and zinc (whose chloride has the formula $ZnCl_2$), it was believed that the formula for indium chloride was $InCl_2$, in which case, in order to preserve the ratio between the two elements, the atomic weight would have to be 37.8 × 2 = 75.6.

When the specific heat of indium was determined,* it was found to be 0.057.

$$\frac{6.4}{0.057} = 112.28$$

Therefore the atomic weight must be raised by one-half, from 75.6 to 113.4, and the formula for the chloride will be $InCl_3$.

The element thallium combines with chlorine in the proportion—

Thallium : chlorine = 203.6 : 35.5.

In some of its compounds thallium exhibits a strong resemblance to potassium, the chloride of which has the formula KCl. If the formula for the thallium chloride is TlCl, the atomic weight of the metal must be 203.6.

In many respects thallium exhibits a striking analogy with lead,

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* Bunsen, 1870.

the chloride of which has the formula, $PbCl_2$. If thallium chloride has a corresponding formula, $TlCl_2$, then the atomic weight of thallium must be raised to 407.2.

When the specific heat of thallium was ascertained,* it was found to be 0.0335.

$$\frac{6.4}{0.0335} = 191.3$$

This result shows that the number 203.6 and not 407.2 is the atomic weight of thallium, and that the chloride has the formula $TlCl$.

Molecular Heat of Compounds.—The capacity for heat of an atom undergoes no alteration when the atom enters into combination with different atoms—in other words, the atomic heat of an element is the same in its compounds. The *molecular heat* of a compound (that is, the product of the molecular weight into the specific heat) will therefore be the sum of the atomic heats of its constituent elements. Hence it is possible to calculate what will be the atomic heat of an element which does not exist as a solid under ordinary conditions; and therefore the atomic weight of such an element, as deduced from other considerations, is capable of verification, by determinations of the molecular heat of various of its compounds: thus—

The specific heat of silver chloride, $AgCl$, is 0.089:—

Specific Heat.		Molecular Weight.		Molecular Heat.
0.089	×	143.5	=	12.77.

The atomic heat of silver = 6.1, therefore, as deduced from this compound, the atomic heat of chlorine is $12.77 - 6.1 = 6.6$.

Again, the specific heat of stannous chloride, $SnCl_2$, is 0.1016:—

Specific Heat.		Molecular Weight.		Molecular Heat.
0.1016	×	189	=	19.2.

The atomic heat of tin is 6.6, therefore the atomic heat of two atoms of chlorine, as deduced from this compound, is $19.2 - 6.6 = 12.6$, giving 6.3 as the atomic heat of chlorine.

The differences that appear in the value, as deduced from various compounds, are lessened, because the errors of the method are more equally distributed, if we divide the molecular heat by the number of atoms in the molecule. Thus, in the

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* Regnault.

two examples quoted, silver chloride consists of two atoms, while the molecule of stannous chloride contains three; if, therefore, the molecular heats of these two compounds are divided respectively by 2 and by 3 we get—

$$\frac{12.77}{2} = 6.38, \text{ and } \frac{19.2}{3} = 6.4,$$

as the value representing the atomic heat of chlorine.

The element calcium combines with chlorine in the proportion—

$$\text{Calcium : chlorine} = 20 : 35.5.$$

If the atomic weight of calcium is 20, the formula will be *CaCl*, whereas if 40 is the atomic weight of the metal, the compound must be represented by the formula $CaCl_2$.

The molecular weight of *CaCl* would be 55.5, that of $CaCl_2$ 111.0.

When the specific heat of the compound was determined, it was found to be 0.1642.. In order, therefore, to decide between the two values for the atomic weight of calcium, we calculate the molecular heat from both of the molecular weights, and divide the result by the number of atoms in the molecule in each case.

On the supposition that Ca = 20, and that *CaCl* represents the chloride:—

$$CaCl \quad . \quad . \quad . \quad \frac{0.1642 \times 55.5}{2} = 4.55.$$

Or, if Ca = 40, and $CaCl_2$ is the formula for the chloride, then—

$$CaCl_2 \quad . \quad . \quad . \quad \frac{0.1642 \times 111.0}{3} = 6.07.$$

The number 6.07, which nearly agrees with the constant 6.4, decides the value 40 as the atomic weight of calcium. The element calcium is one of those metals which it is very difficult to isolate and obtain in a state of purity, but when in recent years the specific heat of this metal was experimentally determined,* it was found to be 0.1704:—

$$0.1704 \times 40 = 6.8.$$

Thus affording direct confirmation of the value 40 for the atomic weight of calcium, which had been deduced from the molecular heat of its compounds.

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* Bunsen.

Deductions based upon molecular heats of compounds are only trustworthy in the case of the most simply constituted compounds.

4. Determination of Atomic Weight from Considerations based on Isomorphism.—It was early observed that certain relations existed between the crystalline forms of compounds and their chemical composition. Mitscherlich found that certain substances having an analogous chemical composition, as, for example, sodium phosphate and sodium arsenate, crystallised in the same geometric form. In the year 1821 he stated his *law of isomorphism* as follows: "The same number of atoms, combined in the same way, give rise to the same crystalline form, which is independent of the chemical nature of the atoms, being influenced only by their number and mode of arrangement." Subsequent investigations, however, have shown that this statement is too general.

In its broad sense as signifying the same crystalline form, isomorphism is found to exist—

1. Between compounds containing the same number of atoms similarly combined, and which bear close chemical analogies to each other.

Isomorphous	Zinc sulphate	$ZnSO_4,7H_2O$.
	Magnesium sulphate	$MgSO_4,7H_2O$.

Isomorphous	Hydrogen disodium phosphate	$HNa_2PO_4,12H_2O$.
	Hydrogen disodium arsenate	$HNa_2AsO_4,12H_2O$.

Isomorphous	Rubidium alum	$Rb_2SO_4,Al_2(SO_4)_3,24H_2O$.
	Potassium chrome alum	$K_2SO_4,Cr_2(SO_4)_3,24H_2O$.
	Potassium aluminium selenium alum	$K_2SeO_4,Al_2(SeO_4)_3,24H_2O$.

2. Between compounds containing a different number of atoms, but which also bear close chemical analogies to one another.

Isomorphous	Ammonium chloride	NH_4Cl.
	Potassium chloride	KCl.

Isomorphous	Ammonium sulphate	$(NH_4)_2SO_4$.
	Potassium sulphate	K_2SO_4.

3. Between compounds containing either the same or a different number of atoms, and which exhibit little or no chemical analogies.

Isomorphous	Sodium nitrate	$NaNO_3$.
	Calcium carbonate	$CaCO_3$.

Isomorphous	Sodium sulphate (anhydrous)	Na_2SO_4.
	Barium permanganate	$BaMn_2O_8$.

Isomorphism of this order, where little or no chemical relations exist between the compounds, is sometimes distinguished as *isogonism*. It must not be supposed, that because two chemically analogous compounds contain the same number of atoms, they will necessarily crystallise in the same form : there are indeed a large number of similarly constituted analogous compounds that do not exhibit isomorphism.

No simple definition of isomorphism is possible, but the following test is generally accepted as a criterion, namely, the power to form either *mixed crystals* or *layer crystals*. Thus, when two substances are mixed in a state of liquidity, and allowed to crystallise, if the crystals are perfectly homogeneous, they are known as *mixed crystals*, and the substances are regarded as isomorphous.

Or when a crystal of one compound is placed in a solution of another compound, and the crystal continues to grow regularly in the liquid, the compounds are isomorphous. Thus, if a crystal of potassium alum (white) be placed in a solution of manganese alum, the crystal continues to grow without change of form, and a layer of amethyst-coloured manganese alum is deposited upon it.

In making use of the law of isomorphism in the determination of atomic weights, it is assumed that the weights of different atoms that can mutually replace each other without altering the crystalline form are proportional to their atomic weights.*

Thus, if we suppose that, in the case of the sulphates of zinc and magnesium, the atomic weight of zinc is known, viz., 65, and that of magnesium is doubtful ; from the fact of the isomorphism of the sulphates it may be premised that the elements are present in proportions relative to their atomic weights. Analysis shows that the proportion is 24 of magnesium to 65 of zinc, therefore 24 is presumably the atomic weight of magnesium.

In this way Berzelius corrected many of the atomic weights which in his day had been assigned to the elements.

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* The group (NH_4) may be regarded as an atom, having the relative weight 18.

CHAPTER VII

QUANTITATIVE CHEMICAL NOTATION

THE use of chemical symbols and formulæ, as a convenient means of representing concisely the qualitative nature of chemical changes, has been explained in chapter iv. We are now in a position to read into these symbols a quantitative significance, which at that stage it would have been premature to explain.

The symbol of an element stands for an atom; but, as we have now learnt, the atoms of the various elements have different relative weights, hence these symbols represent relative weights of matter. The symbol Na signifies 23 relative parts by weight of sodium, O stands for 16 relative parts by weight of oxygen, H for 1 part of hydrogen; in other words, the weight of sodium represented by the symbol Na is 23 times as heavy as that which is conveyed by a symbol H. A chemical equation, therefore, is a strictly quantitative expression, in which certain definite weights of matter are present in the form of the reacting substances, and which reappear without loss or gain in the compounds resulting from the change. In this sense a chemical equation is a mathematical expression. Thus, the equation—

$$\mathrm{Na} + \mathrm{Cl} = \mathrm{NaCl},$$

not only means that an atom of sodium combines with an atom of chlorine and forms 1 molecule of sodium chloride, but it also means

$$\underset{\mathrm{Na}}{23} + \underset{\mathrm{Cl}}{35.5} = \underset{\mathrm{NaCl.}}{58.5}$$

In other words, that sodium and chlorine unite in the relative proportion of 23 parts of the former and 35.5 parts of chlorine, and produce 58.5 parts of sodium chloride.

In the same way, into the equation which expresses the action of sulphuric acid upon sodium carbonate, we read the quantitative meaning of the symbols—

$$\begin{array}{ccccccccc} H_2SO_4 & + & Na_2CO_3 & = & Na_2SO_4 & + & CO_2 & + & H_2O. \\ 2 & & 46 & & 46 & & & & \\ 32 & & 12 & & 32 & & 12 & & 2 \\ \underline{64} & & \underline{48} & & \underline{64} & & \underline{32} & & \underline{16} \\ 98^* & + & 106 & = & 142 & + & 44 & + & 18 \end{array}$$

That is to say, 98 parts by weight of sulphuric acid act upon 106 parts of sodium carbonate, producing 142 parts of sodium sulphate, 44 parts of carbon dioxide, and 18 parts of water. It will be evident that it becomes a matter of the simplest arithmetic to calculate the weight of any product that can be obtained from a given weight of the reacting substances; or *vice versâ*, to find the weight of any reacting substance which would be required to produce a given weight of the product of the action.

Not only is information respecting the quantitative relations by *weight* embodied in a chemical equation, but when gaseous substances are reacting, the equation also represents the volumetric relation between the gases. In order that the volumetric relations may be more manifest, the equations expressing the reactions are written in such a manner as to represent the molecules of the substances.

$$H + Cl = HCl$$

is an *atomic* equation, but as the molecule is the smallest particle which can exist alone, a more exact statement of the chemical change is made, by representing the action as taking place between molecules, thus—

$$H_2 + Cl_2 = 2HCl.$$

From such an equation we see that 1 molecule of hydrogen, or 2 unit volumes, unites with 1 molecule or 2 unit volumes of chlorine, and forms 2 molecules or 4 unit volumes of hydrochloric acid: or again—

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

One molecule, or 2 unit volumes of oxygen, unite with 2 molecules, or 4 unit volumes of hydrogen, and produce 2 molecules of

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[*] The number obtained by adding together the weights of the atoms in a formula is known as a "formula weight," thus 98 is the formula weight of sulphuric acid.

water, which when vaporised, and measured under the same conditions of temperature and pressure, occupy 4 unit volumes. In other words, the number of molecules, in all cases * where gases and vapours are concerned, represent exactly the volumetric relations. In the cases quoted, it will be observed, the same ratio also subsists between the number of *atoms* of the reacting gases and the molecules of the compound, but this is not always the case, for example—

$$\text{Atomic equation, } Hg + 2Cl = HgCl_2.$$

In this equation 3 atoms unite to produce 1 molecule, but the ratio between the volumes is *not* represented by the statement, 1 volume of mercury vapour and 2 volumes of chlorine produce 2 volumes of vapour of mercury chloride.

$$\text{Molecular equation, } Hg + Cl_2 = HgCl_2.$$

By this we see that 1 molecule † (2 unit volumes) of mercury vapour and 1 molecule (2 unit volumes) of chlorine give 1 molecule (2 unit volumes) of vapour of mercury chloride.

Again,

$$P + 3Cl = PCl_3$$

is an atomic equation, showing that 1 atom of phosphorus unites with 3 atoms of chlorine; but it is *not* true that the ratio between the volumes is represented by the statement, 1 volume of phosphorus vapour combines with 3 volumes of chlorine and gives 2 volumes of the vapour of phosphorus trichloride, as will be seen by comparison with the molecular formulæ—

$$P_4 + 6Cl_2 = 4PCl_3.$$

This equation tells us that 1 molecule ‡ (2 unit volumes) of phosphorus vapour combines with 6 molecules (12 unit volumes) of chlorine, producing 4 molecules (8 unit volumes) of phosphorus trichloride vapour.

Knowing the relative densities of gases compared with hydrogen, it is obviously possible, by ascertaining the actual weight in grammes of some definite volume of hydrogen, to calculate the actual weight of any given volume of any other gas.

Two units are in common use, namely—

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* See Dissociation, where apparent exceptions are explained.

† The atomic volume of mercury vapour being equal to 2 unit volumes (p. 44).

‡ The atomic volume of phosphorus is .5 of a unit volume (p. 44).

(1.) The weight of 1 litre of hydrogen, measured at a temperature of 0° C., and under a pressure of 760 mm. of mercury.*

(2.) The volume occupied by 1 gramme of hydrogen, measured under the same conditions.

I. One litre of hydrogen, measured at the standard temperature and pressure, weighs .0896 grammes.† This number is known as the *crith*;‡ and by means of it the weight of 1 litre, and therefore any given volume, of any gas can be deduced: thus, the relative densities of oxygen, nitrogen, and chlorine are 16, 14, and 35.5 respectively, therefore 1 litre of these gases (measured always at the standard temperature and pressure) weighs 16 criths, 14 criths, and 35.5 criths respectively, or—

1 litre of oxygen weighs 16 × .0896 = 1.4336 grammes.
1 „ nitrogen „ 14 × .0896 = 1.2544 „
1 „ chlorine „ 35.5 × .0896 = 3.1808 „

So also with reference to compound gases, where in each case the density is represented by the half of the molecular weight. Thus, the relative densities of hydrochloric acid, ammonia, and carbon dioxide are—

$$HCl\ \frac{1+35.5}{2}=18.25,$$

$$NH_3\ \frac{14+3}{2}=8.5,$$

$$CO_2\ \frac{12+32}{2}=22,$$

and the weights of 1 litre of these gases are therefore—

1 litre of hydrochloric acid = 18.25 × .0896 = 1.6352 gramme.
1 „ ammonia = 8.5 × .0896 = 0.7610 „
1 „ carbon dioxide = 22.0 × .0896 = 1.9712 „

II. The volume occupied by 1 gramme of hydrogen at the standard temperature and pressure is 11.127 litres. As the relative density of oxygen is 16, it obviously follows that 16 grammes

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* This temperature and pressure is chosen as the standard at which volumes of gases are compared. See General Properties of Gases, chapter ix.

† From time to time slightly different values have been given for this constant. The most recent determinations give the number .089873.

‡ From the Greek, signifying a barley-corn, and used symbolically to denote a little weight.

of this gas will also occupy 11.127 litres; in other words, this number 11.127 represents the volume in litres of any gas, which will be occupied by the number of grammes corresponding to its relative density, thus—

14	grammes of	nitrogen . . .	occupy	11.127	litres.
35.5	„	chlorine . .	„	11.127	„
18.25	„	hydrochloric acid	„	11.127	„
22.0	„	carbon dioxide .	„	11.127	„

The number of grammes of a substance, equal to the number which represents its molecular weight, is spoken of as the *gramme-molecule*. The molecular weight of hydrogen = 2, therefore the gramme-molecule of hydrogen (that is, 2 grammes of hydrogen) will occupy $11.127 \times 2 = 22.25$ litres. The molecular weight of oxygen = 32, therefore 32 grammes of oxygen will occupy 22.25 litres; in other words, 22.25 litres is the volume which will be occupied by the gramme-molecule of any gas.

By means of this important constant, 22.25, the volume of any, or all, of the gaseous products of a chemical change (when measured at the standard temperature and pressure) can be deduced directly from the equation representing the change, thus—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

expresses the reaction taking place when zinc is dissolved in sulphuric acid. Just as in the former illustrations it carries the information that 65 grammes of zinc + 98 grammes of sulphuric acid produce 161 grammes of zinc sulphate and 2 grammes of hydrogen. But 2 grammes of hydrogen occupy 22.25 litres, therefore by the solution of 65 grammes of zinc, the volume of hydrogen obtained will be 22.25 litres.

So also in the following equation, which represents the formation of carbon dioxide from chalk (calcium carbonate) by the action upon it of hydrochloric acid—

$$\begin{array}{ccccccccc} CaCO_3 & + & 2HCl & = & CaCl_2 & + & H_2O & + & CO_2. \\ 40+12+48 & & 2(1+35.5) & & 40+71 & & 2+16 & & 12+32 \\ 100 & + & 73 & = & 111 & + & 18 & + & 44 \end{array}$$

100 grammes of chalk, when acted upon by 73 grammes of hydrochloric acid, yield 111 grammes of calcium chloride and 18 grammes of water, and 44 grammes of carbon dioxide.

Carbon dioxide is gaseous, therefore 44 grammes (the gramme-molecule) will occupy, at the standard temperature and pressure, 22.25 litres; hence, by the decomposition of 100 grammes of chalk, 22.25 litres of carbon dioxide are produced.

This chapter may be concluded with one illustration of the methods employed in the exact determination of atomic weights which depends essentially upon the quantitative character of chemical reactions. By the three following processes the atomic weights of chlorine, potassium, and silver may be deduced.

1. By heating a known weight of potassium chlorate, the formula weight of potassium chloride is found—

$$KClO_3 = KCl + 3O.$$

50 grammes of potassium chlorate when heated left a residue of potassium chloride weighing 30.395 grammes. $50 - 30.395 = 19.605$ = grammes of oxygen evolved.

As potassium chlorate contains in its formula weight 3 atoms of oxygen ($16 \times 3 = 48$), we get the expression—

$19.605 : 30.395 = 48 : 74.40$ = formula weight of potassium chloride.

2. By dissolving a known weight of potassium chloride, and adding to it excess of silver nitrate, silver chloride is precipitated, which can be washed and dried and weighed, and from which the formula weight of silver chloride is obtained—

$$KCl + AgNO_3 = AgCl + KNO_3.$$

10 grammes of potassium chloride were found to yield 19.225 grammes of silver chloride; therefore,

$10 : 19.225 = 74.40 : 143.03$ = formula weight of silver chloride.

3. By the direct combination of silver and chlorine, by heating the metal in a stream of the gas, the ratio of chlorine to silver in silver chloride is found:

10 grammes of silver so treated yielded 13.285 grammes of silver chloride; therefore,

$13.285 : 10 = 143.03 : 107.66$ = atomic weight of silver.

Since the formula weight of silver chloride, $AgCl = 143.03$,

therefore, $143.03 - 107.66 = 35.37$ = atomic weight of chlorine.

And since the formula weight of potassium chloride, $KCl = 74.40$,

therefore, $74.40 - 35.37 = 39.03$ = atomic weight of potassium.

CHAPTER VIII

VALENCY OF THE ELEMENTS

WHEN chlorine unites with hydrogen, the combination takes place between one atom of chlorine (relative weight = 35.5) and one atom of hydrogen (relative weight = 1); but when oxygen combines with hydrogen, one atom of oxygen unites with *two* atoms of hydrogen. The compound ammonia consists of one atom of nitrogen, combined with *three* atoms of hydrogen; while one atom of carbon, on the other hand, can unite with *four* atoms of hydrogen.

One atom of chlorine never combines with more than one atom of hydrogen; its affinity for that element is satisfied, or *saturated*, by union with one atom.

The affinity of one atom of oxygen for hydrogen, however, is not satisfied by one atom of that element, but requires two atoms for its saturation; while nitrogen requires three, and carbon four hydrogen atoms, in order to satisfy their respective affinities for this element.

This varying power of combining with hydrogen is seen in a number of other instances: thus, the elements fluorine, bromine, and iodine, resemble chlorine in being only able to unite with one atom of hydrogen. Sulphur, like oxygen, has its affinity for hydrogen saturated by two atoms of that element. Phosphorus and arsenic require three atoms of hydrogen in order to saturate their combining capacity, while silicon resembles carbon in combining with four hydrogen atoms. This combining capacity of an element is termed its *valency*. Elements like chlorine, fluorine, bromine, and iodine, whose atoms are only capable of uniting with one atom of hydrogen, are called *monovalent* (or sometimes *monad*) elements; while those whose atoms combine with two, three, or four hydrogen atoms, are distinguished as di-valent (or dyad), tri-valent (or triad), and tetra-valent (or tetrad) elements. All elements, however, are not capable of entering into combination with hydrogen; in which case, their valency is measured by the number of atoms of some other monovalent element which is capable of satisfying their combining capacity. Thus:—

1	atom of	sodium	combines	with	1	atom	of chlorine,	forming	NaCl.
1	,,	calcium	,,	,,	2	atoms	,,	,,	$CaCl_2$.
1	,,	boron	,,	,,	3	,,	,,	,,	BCl_3.
1	,,	tin	,,	,,	4	,,	,,	,,	$SnCl_4$.
1	,,	phosphorus[*]		,,	5	,,	,,	,,	PCl_5.
1	,,	tungsten	,,	,,	6	,,	,,	,,	WCl_6.

In the combinations of elements with hydrogen alone, no instances are known in which a higher valency is exhibited than that of four; but with chlorine, as here seen, cases are known in which elements exhibit pentavalent and hexavalent characters.

Measured by their combining capacity for hydrogen and chlorine, elements do not, however, always exhibit the same valency: thus, the affinity of phosphorus for hydrogen is satisfied by three hydrogen atoms, whereas one atom of this element can unite with five atoms of chlorine.

As measured by hydrogen, the valency of sulphur is two, the compound that it forms with hydrogen being expressed by the formula SH_2, while, as estimated by its capacity for chlorine, it becomes tetravalent, as seen in the compound SCl_4. As a general rule, however, the highest number of monovalent atoms with which one atom of an element is capable of combining is accepted as representing the valency of that element. Thus, one atom of phosphorus not only combines with five atoms of chlorine, but also with five atoms of fluorine; phosphorus is therefore a pentavalent element.

As measured by hydrogen alone, or by chlorine alone, nitrogen is a trivalent element, for the largest number of these atoms with which one atom of nitrogen can unite is three, as seen in the compounds having the composition NH_3 and NCl_3; nevertheless, one atom of nitrogen is capable of combining with four atoms of hydrogen and one of chlorine, forming the compound NH_4Cl, ammonium chloride, in which the nitrogen atom is pentavalent.

This rule, however, is not always followed; for example, one atom of iodine will unite with three atoms of chlorine, forming the

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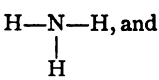
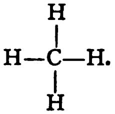
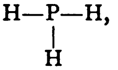
[*] Phosphorus also combines with hydrogen.

compound ICl_3, but iodine is not generally regarded as a trivalent element.*

In symbolic notation, this power possessed by an atom, of uniting to itself monovalent atoms, is often represented by lines, each line signifying the power of combination with one monovalent atom. Thus, in the symbol H—Cl, the line is intended to give a concrete expression to the fact that both hydrogen and chlorine are monovalent elements, and that the affinity of each element for the other is satisfied when one atom of the one unites with one atom of the other. The symbol H—O—H, in like manner, signifies that the oxygen atom is divalent, that its affinity for hydrogen is satisfied only when it has united with two monad atoms. In the same way we may express the facts that nitrogen and carbon, in their combinations with hydrogen, are respectively trivalent and tetravalent, by the symbols  $H-\underset{\underset{\textstyle H}{|}}{N}-H$, and  $H-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}}-H$. These lines are merely a convenient symbolic expression for the operation of the force of chemical affinity ; their length and direction bear no meaning.† The power to combine with one monovalent atom is sometimes spoken of simply as one *affinity :* thus it is said that in the compound having the composition PH_3, or  $H-\underset{\underset{\textstyle H}{|}}{P}-H$, three of the *affinities* of the phosphorus atom are saturated, and that two *affinities* still remain unsatisfied, phosphorus, as already stated, being a pentavalent element.

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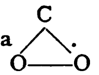
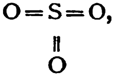
* See Iodine, Compounds.

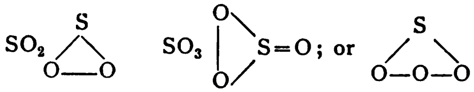
† The student cannot be too often warned against attaching any materialistic significance to these lines. The use of this convention is always attended with the danger that the beginner is liable to fall into the error of regarding these lines as representing in some manner fixed points of attachment, or links, between the atoms. It must be remembered, therefore, that these lines not only have no materialistic signification, but they must not even be regarded as conveying any statical meaning. The atoms are undergoing rapid movements with respect to each other, which movements are in some way governed by the chemically attractive force exerted by the individual atoms upon one another ; and the molecule will be more correctly considered, if we regard its atoms as being held together in a manner resembling that by which the numbers of a cosmical system are bound together. The lines simply denote that the atoms are held to each other by the attractive force which we call chemical affinity.

Compounds of this order, in which one of the elements has still unsatisfied affinities, are called *unsaturated* compounds.

In its power to satisfy the affinities of an element, a divalent atom is equal to two monovalent atoms : thus, when the affinities of the tetravalent carbon atom are saturated with oxygen, the molecule contains two atoms of oxygen, which may be symbolically expressed thus, $O=C=O$, in which the four affinities of the carbon (represented by the four lines) are satisfied by the two divalent atoms of oxygen. Carbon, however, combines with a smaller proportion of oxygen, forming the compound carbon monoxide, CO. The carbon atom in this case is divalent, as expressed by the formula $C=O$, and this substance is also an unsaturated compound.

The number of divalent atoms with which an element can unite cannot, however, be taken as a safe criterion or measure of the valency of that element in cases where that number is greater than 1 ; for example, in such a compound as calcium oxide, CaO, we regard the two affinities of the divalent atom of oxygen as being satisfied by two affinities possessed by the calcium, and express this belief in the formula $Ca=O$, and regard the calcium as divalent. In the same way, in carbon monoxide, CO, the carbon being united with one atom of the divalent element oxygen is itself divalent in this compound ; but in the case of carbon dioxide, where the carbon atom is united with two atoms of divalent oxygen, we are not justified in asserting that the atoms are united, as represented by the formula $O = C = O$, in which the four affinities of carbon are represented as saturated with oxygen. There exists no positive proof that the carbon is not divalent in this compound, and that the molecule does not consist of three divalent atoms united, as shown in the formula . From the fact, however, that carbon forms a compound with four atoms of hydrogen, and another with four atoms of chlorine, we know that this element is tetravalent, and therefore we *believe* that in carbon dioxide it is also tetravalent.

Again, as measured by its compound with hydrogen, sulphur is divalent ; while with chlorine it forms SCl_4. But sulphur unites with oxygen, forming the two compounds sulphur dioxide, SO_2, and sulphur trioxide, SO_3. If it be assumed that in these molecules the whole of the oxygen affinities are satisfied with sulphur, then the symbolic representation of these oxides will be $O = S = O$, and  $O=\underset{\underset{O}{\|}}{S}=O$, the sulphur being in one case tetravalent and in the other hexavalent. There is, however, no *positive* proof that the affinities of one oxygen atom are not partially satisfied by union with another oxygen atom, and that the valency of the sulphur is higher than either two or four, as seen in the alternative formulæ,



Chemists *believe*, however, that in these two oxides the sulphur functions in the one case as a tetravalent, and in the other as a hexavalent element; and this belief is strengthened by the recent discovery (Moissan) of a fluoride having the composition SF_6, in which the hexavalent character of sulphur is unquestionable.

It will be evident from these considerations, that in many cases the valency of an element is a variable quantity, depending partly upon the particular atoms with which it unites. It is also found that it is dependent in many instances upon temperature and upon pressure. Thus, between a certain limited range of temperature, one atom of phosphorus combines with five atoms of chlorine in the compound PCl_5, but above that limit two atoms of chlorine leave the molecule, and the phosphorus becomes trivalent. Again, if hydrogen phosphide, PH_3, be mixed with hydrochloric acid, HCl, and the mixed gases be subjected to increased pressure, the gases combine and form a solid crystalline compound known as phosphonium chloride, PH_4Cl, in which the phosphorus atom, being united with five monovalent atoms, is pentavalent. When the pressure is released an atom of hydrogen and an atom of chlorine leave the molecule, and the phosphorus returns to its trivalent condition.

A compound, in whose molecules there is an atom which for the time being is not functioning in its highest recognised valency, often exhibits a readiness to unite with additional atoms to form new compounds: thus ammonia combines eagerly with hydrochloric acid, forming ammonium chloride—

$$NH_3 + HCl = NH_4Cl.$$

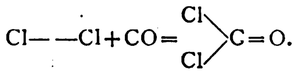
Carbon monoxide unites directly with chlorine to form carbonyl chloride—

$$CO + Cl_2 = COCl_2.$$

Carbon monoxide also combines with an additional atom of oxygen, and gives carbon dioxide, thus—

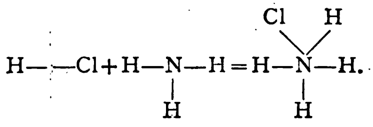
$$2CO + O_2 = 2CO_2.$$

In this last action it will be seen that the molecule of carbon monoxide, in being converted into the dioxide, takes up one atom of oxygen; but as the molecule of oxygen is the smallest isolated particle, it follows that the two atoms contained in such a molecule must first separate, and each one then furnishes the requisite additional oxygen for one molecule of carbon monoxide. In the union of carbon monoxide with chlorine, and of ammonia with hydrochloric acid, are we to suppose that the same action takes place? That is to say, do the two atoms in the molecule of chlorine separate from each other and unite with carbon, thereby satisfying its tetrad valency, in the manner here expressed?—



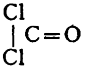
$$\mathrm{Cl{-}\;{-}Cl + CO = \begin{array}{l} Cl\diagdown \\ \qquad\ \ C{=}O. \\ Cl\diagup \end{array}}$$

And in the case of ammonia and hydrochloric acid, do the hydrogen and chlorine atoms part, and each unite with the nitrogen atom, thereby raising it from the trivalent to the pentavalent condition? thus—

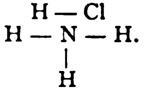


$$\mathrm{H{-}\;{-}Cl + H{-}\underset{\textstyle H}{\underset{|}{N}}{-}H = H{-}\overset{Cl\ \ \ H}{\overset{\diagdown\,\diagup}{\underset{\textstyle H}{\underset{|}{N}}}}{-}H.}$$

Or are we to suppose that the two molecules, without losing their integrity, become held together as independent molecules, by virtue of the unsatisfied affinities of the carbon, or the nitrogen, as the case may be, in which case the compounds might be represented thus—



$$\begin{array}{l} \mathrm{Cl} \\ \mid \mathrm{C{=}O} \\ \mathrm{Cl} \end{array}$$



$$\begin{array}{c} \mathrm{H - Cl} \\ \mathrm{H - N - H.} \\ \mid \\ \mathrm{H} \end{array}$$

This question would be settled by determining the vapour-density of the compound. If, for instance, we were to find the vapour-density of ammonium chloride to be 26.75, then the compound having the composition NH_4Cl would have the normal molecular volume, that is, its molecule would occupy two unit volumes,* and the conclusion would be that the vapour consisted of single molecules of the composition represented by the formula NH_4Cl. But ammonium chloride at ordinary temperatures is a solid, and when heated to the temperature necessary to convert it into vapour its molecules break up into separated molecules of the two original gases—ammonia, NH_3, and hydrochloric acid, HCl.† So that we are unable to gain any information in this direction as to the mode in which the atoms are disposed in the compound. When the two gases are brought together under ordinary conditions, they combine with the evolution of considerable heat, owing to loss of energy; this is taken as evidence that true chemical action, in the sense of atomic rearrangement, has resulted, hence it is believed that in this compound the nitrogen is united with the five monovalent atoms, and consequently is pentavalent.

In the case of carbonyl chloride, $COCl_2$, the vapour-density can be ascertained, this compound existing in the gaseous condition at the ordinary temperature. Its vapour-density, determined by experiment, is found to be 50.6. This number, divided into the molecular weight of the compound having the composition $COCl_2$, gives practically the number 2 as the molecular volume of the compound. Hence we conclude that these four atoms constitute a single molecule.

There are a number of combinations, however, in which mole-

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* See p. 43.

† See Dissociation, p. 89.

cules of different compounds unite, that do not so readily admit of explanation, because in neither of the molecules is there any atom functioning in a lower state of valency than that which it is known to be capable of. For example, the monovalent elements fluorine and hydrogen form the compound hydrofluoric acid, HF; fluorine also combines with the monovalent element potassium, forming potassium fluoride, KF. Both of these compounds come under the head of *saturated* compounds, in the sense that neither of them contains an atom which is known to be capable of exercising a higher valency than it exhibits in these compounds. Nevertheless these two molecules unite together and form a definite chemical compound, known as hydrogen-potassium fluoride.

Again, the divalent element zinc combines with two atoms of the monad element chlorine, forming zinc chloride, $ZnCl_2$; the two monovalent elements sodium and chlorine also combine, giving the compound sodium chloride, NaCl. Both of these substances must be regarded as saturated compounds, and yet they unite with each other, forming a distinct chemical compound, known as sodium zinc chloride. Such compounds as these are known as *double salts*, and examples might be multiplied almost indefinitely. A similar union of molecules, where the recognised valency of the atoms is all satisfied, is seen in a large number of compounds containing water of crystallisation;* for example, the divalent element copper, in combination with two atoms of chlorine, forms cupric chloride, $CuCl_2$. The divalent element oxygen, in combination with two hydrogen atoms, forms water, H_2O. When cupric chloride crystallises from aqueous solution, each molecule of the chloride unites to itself two molecules of water, which is therefore termed water of crystallisation.

In chemical notation, it is usual to represent compounds of this order by placing the formulæ of the different molecules that have entered into union in juxtaposition, with a comma between; accordingly, the examples here quoted would be indicated thus—

Hydrogen potassium fluoride . .	HF,KF.
Sodium zinc chloride	$ZnCl_2,NaCl$.
Crystallised cupric chloride . .	$CuCl_2,2H_2O$.

Combinations of this order are by no means confined to the

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* See page 216.

union of *two* kinds of molecules, as the following examples will serve to show :—

Platinum sodium chloride .	. $PtCl_4,2NaCl,6H_2O$.
Mercuric potassium chloride	. $2HgCl_2,KCl,2H_2O$.

At the present time our knowledge of the nature of the union between these various molecules is too imperfect to admit of any precise explanation ; such compounds are frequently distinguished as *molecular combinations.*

It is quite possible that the unit which has been adopted for estimating valency, namely, 1 monovalent atom, is after all only an extremely rough and crude measure, which is incapable of appreciating smaller differences of combining capacity that may, and most probably do, exist. Its use may be compared to the adoption of a single unit, say 1 gramme, for the estimation of mass or weight ; when, if a given quantity of matter has a weight equal to 1 gramme, but less than 2 grammes, its weight would be 1 ; if greater than 2 grammes, but less than 3, then its weight would be 2—a method of estimating which tacitly assumes that no intermediate weights of matter between the various multiples of the selected unit are possible. There is no evidence to show that the combining capacity of an element is *exactly* expressed by simple multiples of a monovalent atom.

For example, 1 hydrogen atom unites with 1 chlorine atom, that is to say, with a mass of chlorine weighing 35.5 times its own weight ; and we say that the *mutual* affinities of these atoms are satisfied. But for anything we know to the contrary, an atom of hydrogen may have an affinity for chlorine which would enable it to unite with a mass of chlorine weighing 40 or 45 or 50 times its own weight, but *not* a mass weighing 71 (35.5 × 2) times its own. But since a mass of chlorine 35.5 times the weight of a hydrogen atom is the smallest quantity that is ever known to take part in a chemical change, is the chemically indivisible mass we call an atom, it follows that as the hydrogen atom has not sufficient combining capacity to unite with 2 atoms, it is compelled to be satisfied with 1. It might still, however, retain a *residual combining capacity.* Or the residual combining capacity may be lodged in the chlorine atom, which may be conceived as being able to unite with a greater weight of hydrogen than is represented by 1 atom, but not so much as that of 2 atoms.

Each of the elements fluorine, chlorine, bromine, and iodine unites with 1 atom of hydrogen, and we represent their compounds in a similar manner, thus—

$$H - F ; \quad H - Cl ; \quad H - Br , \quad H - I ;$$

but we make an enormous assumption if we suppose that in each of these compounds the mutual affinities of the atoms is equally satisfied.

The trend of modern thought, however, lies in the direction of an electrical interpretation of valency. The fact that atoms are always associated with fixed and definite charges of electricity, that valency, indeed, could be measured in terms of electric units (the outcome of Faraday's Law, chap. xi.) seemed at one time only to emphasise the difficulty of explaining such cases as those above mentioned; but the more recent developments in this region of physics have led to modified views as to the nature of the bond which unites atoms together. Stated in briefest outline, this chemical "bond" or unit of affinity, which formerly has been regarded in the light of a single line of force—a fraction of a bond being considered as altogether inadmissible—is now regarded as a *bundle* of lines of force (a Faraday bundle). Under appropriate conditions, such as the proximity of suitable molecules or ions, it is conceived that some strands of the bundle may become loosened from one of the attached atoms and thus become available for attraction by similar wandering strands from other molecules. Obviously, therefore, this view admits of practically an unbroken gradation in degrees of chemical affinity. Instead, therefore, of *residual* affinity, we now have varying fractions of the total bundle of lines of force which in its entirety constitutes the chemical "bond"; the two conceptions are not very widely different.

CHAPTER IX

GENERAL PROPERTIES OF GASES

UNDER the head of the general properties of gases it will be convenient to consider the following subjects :*—

1. The relation of gases to heat.
2. The relation of gases to pressure.
3. The liquefaction of gases.
4. Diffusion of gases.
5. The kinetic theory of gases.

The Relation of Gases to Heat.—The fact that substances expand when heated, and again contract upon being cooled, was observed in very early times. The fact also that all substances do not undergo the same alterations in volume when subjected to the same changes of temperature has been long known ; but it was not until the beginning of the nineteenth century that it was proved by Charles and Gay-Lussac that all gases expanded and contracted equally when exposed to the same alterations of temperature. This law is generally known as the Law of Charles, and may be thus stated : *When a gas is heated, the pressure being constant, it increases in volume to the same extent whatever the gas may be.*

The increase in bulk suffered by 1 volume of a gas in being heated from 0° to 1° is termed the coefficient of expansion, and if the law of Charles is true all gases will have the same coefficient.

Modern research has shown that the law of Charles is not *absolutely* true, and the extent to which gases deviate from the strict expression will be seen from the coefficients of expansion given in the following table :—

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* The study of these subjects belongs more especially to the science of physics or chemico-physics. For fuller information on these points than can be included within the scope of this book students are referred to special treatises on physics.

Air	.003665
Hydrogen	.003667
Carbon monoxide	.003667
Nitrogen	.003668
Nitrous oxide	.003676
Carbon dioxide	.003688
Cyanogen	.003829
Sulphur dioxide	.003845

It will be noticed that the first four gases have almost the same coefficient of expansion: these gases are all very difficult of liquefaction, and it will be seen that the coefficient rapidly rises in the case of the other gases, which are easily liquefied.

For purposes of ordinary calculation it is usual to adopt the coefficient of expansion of air as applicable to all gases. It will be obvious that since the volume of a gas is affected by alterations of temperature, it becomes necessary, when measuring the volume of a gas, to have regard to the particular temperature at which the measurement is made, and in order to compare volumetric measures they must be all referred to some standard temperature. This standard temperature is by general consent 0° C.

Taking the fraction .003665, therefore, for the coefficient—

1 volume of a gas at 0° becomes $1 + .003665$ volumes at 1°
1 " " 0° " $1 + .003665 \times 2$ " 2°
or 1 " " 0° " $1 + .003665\,t$ " t°

Therefore the volume at t° equals the volume at 0° multiplied by $1 + .003665\,t$. Let v be the volume at t°, and v_0 the volume at 0°, then—

$$v = v_0(1 + .003665\,t),$$

and conversely the volume at 0° equals the volume at t° divided by $1 + .003665\,t$—

$$v_0 = \frac{v}{1 + .003665\,t}$$

The vulgar fraction equivalent to .003665 is $\frac{1}{273}$. 273 volumes at 0° become $273 + t$ at t°.

What is known as the *absolute temperature* of a substance is the number of degrees above −273° C. Taking this point as the zero, the absolute temperature of melting ice, for example, will be 273°. Charles' law, therefore, may be thus stated: *The volume of any* *gas, under constant pressure, is proportional to the absolute temperature.*

The Relation of Gases to Pressure.—The effect of increase of pressure upon a gas is to diminish its volume. The law which connects the volume occupied by a gas, with the pressure to which it is subjected, was discovered by Robert Boyle (1661), and is known as Boyle's Law. It may be thus stated: *The volume occupied by a given weight of any gas is inversely as the pressure.* The general truth of this law may readily be illustrated by subjecting a gas to varying pressures, and it will be seen that when the pressure is doubled the volume of gas is reduced to one-half, and so on.

Just as in the case of the law of Charles, modern investigations have shown that the law of Boyle is not a mathematical truth. It is found not to be absolutely true of any gas, for, with the exception of hydrogen, all gases are more compressible than is demanded by the law. Hydrogen deviates from the law in an opposite sense, in that it requires a higher pressure than the law would indicate, in order to reduce a volume of it to a given point. These deviations from Boyle's law are explained by the operation of two causes; first, the attraction exerted by gaseous particles upon each other; second, the fact that increased pressure diminishes the space *between* the molecules, and not the actual space *occupied by* the molecules of a gas. When the former cause predominates, the gas deviates from the law by being more compressible; in the case of hydrogen the second cause operates more powerfully. (See Kinetic Theory of Gases.) For ordinary purposes of calculation the law of Boyle may be regarded as true.

As the volume of a given weight of gas is so intimately related to the pressure, and as the atmospheric pressure is variable, it becomes necessary, in all quantitative manipulation with gases, to know the actual pressure under which the gas is at the time of measurement, and to refer the volume to a standard pressure. The pressure that has been adopted as the standard is that of a column of mercury 760 mm. in height. (See Atmosphere.)

If v equals the volume of gas measured at p pressure, and v_0 the volume at the standard pressure, then

$$v_0 = \frac{vp}{760}.$$

In practice it is most usual to make both correction for temperature and pressure together; then v_0 being the volume at the standard temperature and pressure, we get

$$v_0=\frac{v}{1+.003665\,t}\cdot\frac{p}{760}^{*}.$$

The Liquefaction of Gases.—Under certain conditions of temperature and pressure, the law of Charles and the law of Boyle both completely break down. According to the law of Charles, 100 c.c. of a gas at 0° C. should occupy 96.4 c.c. if the temperature were lowered to –10°. If 100 c.c. of the gas sulphur dioxide at 0° C. be confined in a glass tube standing in mercury, and the gas be cooled to –10° by surrounding the tube with a freezing mixture, it will be found that the volume of gas, instead of occupying 96.4 c.c., has been reduced to a few cubic centimetres only, and that the surface of the mercury in the tube is wet owing to the presence of a minute layer of a colourless liquid upon it. In this case the law of Charles has broken down, and the sulphur dioxide has passed from the gaseous to the liquid state.

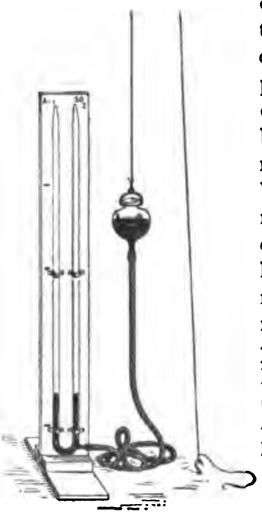

FIG. 1.

Similarly, according to the law of Boyle, 100 c.c. of a gas measured at the standard pressure should occupy 25 c.c. when exposed to a pressure of four additional atmospheres. If 100 c.c. of the gas sulphur dioxide be enclosed in one limb of a long U-tube, as shown in Fig. 1, the other limb being filled with air, and the two gases be simultaneously exposed to increased pressure by raising the mercury reservoir, it will be seen that at first the gases in both tubes are compressed equally. As the pressure approaches three atmospheres, however, the mercury will be seen

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[*] The student should familiarise himself with the method of calculating the changes of volume suffered by gases, by changes of temperature and pressure, by working out a number of examples such as the following:—

1. If 30 litres of gas are cooled from 25° to 0°, what is the diminution in volume, the pressure being constant? *Ans.* 2.51 litres.

2. If a litre of air at 0° weighs 1.293 grammes when the barometer is at

to rise much more rapidly in the tube containing the sulphur dioxide, and when the mercury reservoir has been raised to such a height that the gases are subjected to four atmospheres, the sulphur dioxide will have completely broken down, and will be entirely converted into a few drops of liquid, which appear upon the surface of the mercury. The air meantime, in the other limb, will be found to occupy 25 c.c., as that gas at that pressure obeys Boyle's law almost absolutely. We see, therefore, that at a certain temperature and at a certain pressure the gas sulphur dioxide begins rapidly to depart from the laws of Charles and Boyle, and ultimately passes into the liquid condition.

All known gases, when exposed to certain conditions of temperature and pressure, conditions which are special for each different gas, will pass from the gaseous to the liquid state; and as the point at which liquefaction takes place is approached, the departures from Boyle's law become more and more pronounced.

The first substance, recognised as being under ordinary conditions a true gas, that was transformed into the liquid condition was chlorine, which was liquefied in the year 1806 by Northmore. The true nature of this liquid was not understood until Faraday investigated the subject.

In his earlier experiments Faraday's method consisted in sealing into a bent glass tube (Fig. 2) substances which, when heated, would yield the gas; the substances being contained in one limb of the tube, and the empty limb being immersed in ice. The pressure exerted by the gas thus generated in a confined space was sufficient to cause a portion of it to condense to

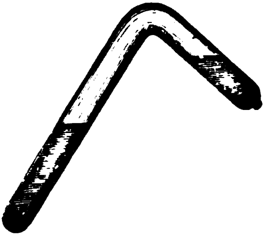
FIG. 2.

760 mm., what will be the weight of a litre of air at 27°, the barometer standing at the same height? *Ans.* 1.177 grammes.

3. What will be the weight of a litre of air at 42° when the barometer stands at 735 mm.? *Ans.* 1.084 grammes.

4. Air at a temperature of 15° is enclosed in a vessel and heated to 93°. Compare the pressure of the enclosed air with that of the atmosphere. *Ans.* As 61 : 48.

5. What will be the volume, at the standard temperature and pressure, of 500 c.c. of hydrogen, measured at 20°, and under a pressure of 800 mm.? *Ans.* .490 c.c.

the liquid state, and the liquid collected in the cooled limb. In this way Faraday liquefied such gases as chlorine, sulphur dioxide, ammonia, cyanogen. In his later experiments Faraday compressed the gas by means of a small compression pump, and at the same time applied a low degree of cold, and by so doing he succeeded in liquefying carbon dioxide, hydrochloric acid, nitrous oxide, and other gases. There were a number of gases, however, which Faraday found it impossible to liquefy, such as hydrogen, oxygen, nitrogen, marsh gas, nitric oxide, carbon monoxide, &c. It became the custom to call these *permanent gases*, and this term was applied to them until the year 1877.

In that year it was proved by Pictet, and independently by Cailletet, that under sufficiently strong pressure, and a sufficiently low degree of cold, the so-called permanent gases could in the same way be reduced to the liquid condition. Pictet's method was in principle the same as that employed by Faraday, the difference being that with the machinery at his disposal he was able to employ enormously increased pressure and a greater degree of cold. For the liquefaction of oxygen, a quantity of potassium chlorate was heated in a strong wrought-iron retort, to which was connected a long horizontal copper tube of great strength and small bore. At the extreme end of this tube there was a pressure gauge capable of indicating pressures up to 800 atmospheres, and a stop-cock. The tube was cooled by being contained in a wider tube, through which a constant stream of liquid carbon dioxide, at a temperature of $-120°$ to $-140°$, was caused to flow.

The machinery employed to maintain this flow of liquefied carbon dioxide was somewhat elaborate, consisting of condensing and exhaust pumps for liquefying and rapidly evaporating sulphur dioxide, and similar condensing and exhaust pumps for liquefying and rapidly evaporating carbon dioxide : the sulphur dioxide being merely the refrigerating agent used to assist the liquefaction of the carbon dioxide. This machinery was driven by two eight-horse-power engines. As the potassium chlorate was heated and oxygen evolved, the internal pressure in the retort and copper tube rapidly rose, and its amount was indicated by the gauge.

When the stop-cock upon the end of the tube was opened, liquid oxygen was forcibly driven out in the form of a jet.

In the method employed by Cailletet, the pressure to which the gas is subjected is obtained by purely mechanical means. The gas to be liquefied is introduced into a glass tube (Fig. 3), the narrow end of which consists of a strong capillary tube. The tube carries a metal collar, which enables it to be secured in position in the strong steel bottle (Fig. 4), by means of a nut, E′ (Fig. 5), which screws into the mouth. The bottle, which is partially filled with mercury, is connected by means of a flexible copper tube of fine bore with a small hydraulic pump, by means of which water is forced into the steel bottle. The water so driven in forces the mercury up into the glass tube T, and thereby compresses the contained gas. In this way a pressure of several hundred atmospheres may be applied to the gas. In his earlier experiments Cailletet depended almost entirely for the refrigeration he required upon the fact, that when a gas is allowed suddenly to expand it undergoes a great reduction in temperature. This method of cooling may be termed *internal* refrigeration. In the case of oxygen, the gas was first subjected to a pressure of 300 to 400

FIG. 3.

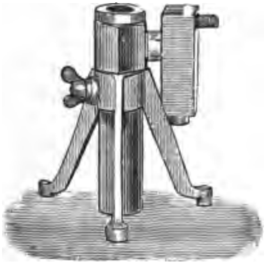

FIG. 4.

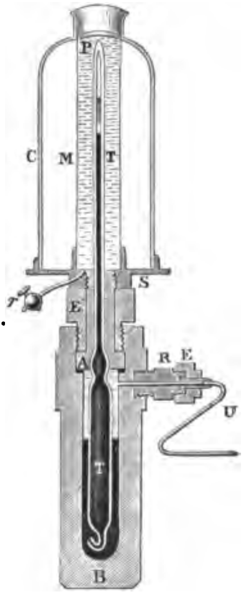

FIG. 5.

atmospheres, and was then allowed suddenly to expand by a rapid release of the pressure. The result of the sudden expansion was to momentarily lower the temperature of the gas to such a point that the tube was filled with a fog, or mist, consisting of liquid particles of oxygen.

This principle, namely, the self-cooling of a gas by its own sudden expansion, has recently been applied for the liquefaction of oxygen in large quantities. When oxygen under considerable pressure, say 120 atmospheres, is allowed to escape from a fine orifice at the end of a long pipe, the issuing gas suddenly expands, and thereby its temperature is greatly lowered. If this self-cooled gas is made to sweep over the pipe from which it is escaping, it will cool the pipe, and therefore lower the temperature of the remaining gas before it issues. In this way the cooling effect becomes cumulative, the initial temperature of the gas before it escapes being continually brought lower and lower, until at last the point is reached at which the oxygen is liquefied.[*]

If the oxygen be first cooled to about −80° by means of solid carbon dioxide, then in a *few minutes*, by the further cooling due to its own expansion, the temperature will fall below the boiling-point of oxygen, and the liquefied gas be obtained.

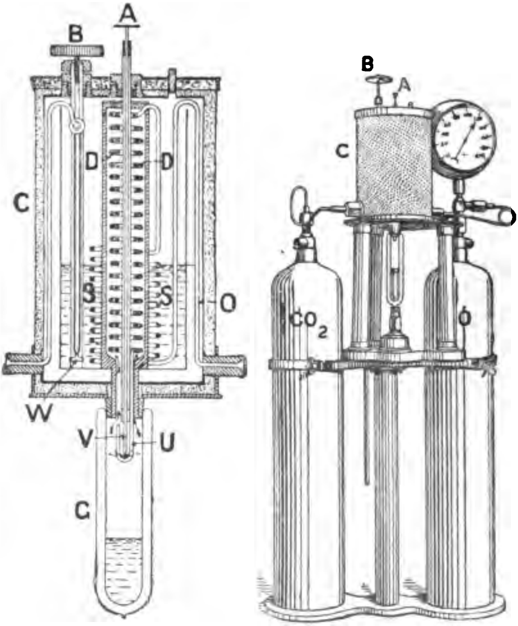

FIG. 6.

The apparatus for the purpose is shown in Fig. 6.[†] Oxygen

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[*] Linde, *The Engineer*, Oct. 4, 1895.

[†] Designed by Dewar; constructed by Messrs. Lennox, Reynolds & Fyfe.

under a pressure of 120 to 140 atmospheres is passed through a series of spirals of fine copper pipe contained in the chamber C, which is encased in a non-conducting jacket of cork-dust. The gas enters by the pipe O (seen in the enlarged section), and passes through the spiral S S, which is immersed in a mixture of alcohol and solid carbon dioxide (the liquid carbon dioxide from the reservoir being admitted into the alcohol through the valve W, which is regulated by the screw B). The oxygen thus cooled passes through the double spiral pipe D D, which ultimately extends through the bottom of the chamber, and terminates in a stirrup, U, the short end of which is closed. In the bend of this stirrup there is a fine hole, which can be closed or opened at will by the pointed end of the rod V, connected to the screw A. On opening this valve, the oxygen, already cooled to about −80°, escapes from the hole under a pressure of 120 to 140 atmospheres. It instantly expands, and is thereby cooled still lower. This cold gas is prevented from escaping at once into the atmosphere by the glass tube G, but is compelled to rush upwards (as shown by the arrows), and, sweeping past the double spiral D D, cools this pipe, and therefore the succeeding portions of issuing oxygen. In a few minutes the temperature of this pipe is thereby brought so low, that the further cooling of the gas by its expansion causes the liquefaction of a portion of it, and a fine spray of liquid is seen to spurt out from the hole. This spray quickly increases in quantity, and rapidly collects as a clear liquid in the glass tube G. This tube is double-walled, the space between the walls being perfectly vacuous. In such a vessel the liquid oxygen may be kept for a considerable time, evaporating only very slowly in spite of its extremely low boiling-point, as it has been found that such a vacuous envelope forms the most perfect non-conductor.

The instruments designed by Linde in Germany, and by Hampson in England, and known as *air-liquefiers*, are constructed on precisely similar principles. In this case, however, the preliminary cooling by means of solid carbon dioxide is dispensed with; for instead of a limited and comparatively small supply of compressed gas in a steel cylinder, an unlimited supply of air is delivered into the machine, under a pressure of 120 to 160 atmospheres, by means of powerful compression pumps driven by an engine.

By an extension of the same principles hydrogen was first successfully liquefied in 1898. In this case, however, the gas requires to be previously cooled to about − 200° before expansion is allowed to take place. By utilising the low temperatures which can be obtained by means of boiling liquefied gases, it has now become possible to liquefy all the known gases by cold alone, that is, without the application of pressure; in other words, their temperatures can be brought down *below* their boiling-points, under which circumstances they must obviously assume the liquid state. For example, liquefied ethylene boils at − 103.5°; if, therefore, a stream of nitrous oxide is passed through a tube immersed in a bath of liquid ethylene, the nitrous oxide will be cooled below its boiling-point (− 89.8°), and will consequently be reduced at once to the liquid state. Again, liquid oxygen boils at − 182.5°. This boiling liquid therefore is sufficiently cold to cool marsh gas below *its* boiling-point, namely, − 164.7°, and therefore to cause its liquefaction.

Moreover, by the rapid evaporation of liquid oxygen the temperature may readily be lowered to the point at which air will liquefy. Thus, if a quantity of liquid oxygen in the glass tube O (Fig. 7), which is provided with a vacuous envelope, V, be made to boil rapidly by putting the pipe P in connection with an exhaust-pump, the temperature quickly falls to − 200°, when air itself becomes liquefied without the application of pressure; and drops of liquid air quickly collect upon the walls of the inner empty tube, N, which is freely open to the atmosphere. In this way considerable quantities of liquefied air can be collected in a few minutes.

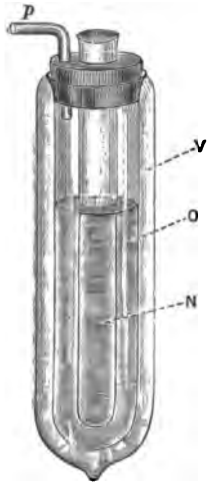

FIG. 7.

By means of boiling liquid hydrogen the low temperature of − 253° has been reached, at which temperature all other known gases, except perhaps helium, are frozen to the solid state. The lowest temperature yet obtained by the rapid evaporation of solid hydrogen is − 260° (Dewar).

The Critical Point.—As far back as the year 1869, it was shown by Andrews that when liquid carbon dioxide was heated to a particular temperature, it passed from the liquid to the gaseous state, and that no additional pressure was able to condense it again so long as the temperature remained at or above that point. This particular temperature is called the *critical point*, or the *critical temperature* of the gas. In the case of carbon dioxide this critical temperature is 31.35°, and in order that this gas may be liquefied by pressure, it is an essential condition that the temperature be below that point ; above 32° no pressure is capable of bringing about liquefaction. All gases have a critical temperature, which is special for each gas, and until the temperature of the gas be lowered to that point, liquefaction is impossible. The critical temperatures of the different gases vary through a very wide range : thus, the critical temperature of hydrogen is as low as −238°, while that of sulphur dioxide is +155.4°. In the third column of the table of physical constants on page 80 the critical temperatures of a number of the more common gases are given.*

The gases in this list, from ethylene downwards, all have their critical temperatures so high that there is no difficulty in cooling them below these points. These are the gases which were first reduced to the liquid state. The first five upon the list have very low critical temperatures ; these are the very gases which for so long resisted all attempts to liquefy them, and which were on that account called *permanent* gases. We now know that the failure to obtain them in the liquid state was owing to the fact that the relation between the critical temperature and the point of liquefaction was not fully realised. Just as carbon dioxide cannot be liquefied unless its temperature be brought down to 31.35°, so oxygen resists liquefaction under the highest possible pressures, until its temperature be lowered to −118.8°, the critical temperature of oxygen.

The critical temperature of a gas is sometimes spoken of as the *absolute boiling-point.*

Critical Pressure.—The particular pressure that is required to liquefy a gas at its critical temperature is called the *critical pressure.* Thus the pressure necessary to liquefy oxygen, when the temperature has been lowered to −118.8°, is 58 atmospheres ; while that required to condense chlorine at its critical point, viz., +141°, is 84 atmospheres. At temperatures *below* the critical temperatures a gas liquefies under *less* pressure than the *critical*

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* For the constants for the gases of the Argon family see page 271. It may be well to remind the student that such constants as are here tabulated are obtained from measurements involving very great experimental difficulties, and that consequently they are always liable to revision. The values here given are from the most recent determinations.

pressure, until when the temperature is lowered to the boiling-point of the gas it passes into the liquid state without the application of any external pressure. The following table contains the most recently determined physical constants of a number of common gases :—

TABLE OF PHYSICAL CONSTANTS.

	Boiling-Point.	Melting-Point.	Critical Temp.	Critical Pressure.	Density at Boiling-Point.
Hydrogen . .	−253°	−257°	−238°	15.3 Ats.	0.06
Nitrogen . . .	−195.5°	−213°	−149°	27.5 ,,	0.791
Carbon monoxide .	−190°	−207°	−136°	33.5 ,,	...
Oxygen . . .	−182.5°	−223°	−118.8°	58.0 ,,	1.131
Methane (marsh gas)	−164.7°	−184°	− 82°	55.8 ,,	0.416
Ethylene . . .	−103.5°	−169°	+ 9°	58.0 ,,	0.571
Nitrous oxide . .	− 89·8°	−102.7°	+ 37°	... ,,	...
Acetylene . . .	− 82·7°	...	+ 35°	61 ,,	...
Carbon dioxide .	− 80°	...	+ 31.35°	72.3 ,,	...
Ammonia . . .	− 38.5°	− 75.5°	+131°	113 ,,	...
Chlorine . . .	− 33.4°	...	+141°	84 ,,	1.507
Sulphur dioxide .	− 10°	...	+155.4°	78.9 ,,	...

From the figures given in this table it will be seen that the critical pressure (which is the pressure required to liquefy a gas *at the highest temperature at which pressure can possibly cause liquefaction*) is in most cases comparatively small. In only one instance, namely, ammonia, is it over 100 atmospheres, and falling in the case of hydrogen as low as 15.3 atmospheres. The enormous pressures, therefore, amounting often to many hundred atmospheres, which some of the earlier experimenters employed in attempting to effect the liquefaction of the so-called permanent gases, are thus seen to have been efforts in an entirely wrong direction. It was not greater *pressure* that was required, but the means of cooling the gases to a sufficiently low temperature.

In ordinary language such a gas as chlorine is spoken of as an *easily* liquefied gas, while oxygen would be described as a *difficultly* liquefied gas. Strictly speaking, however, and considering them from a comparable standpoint, it would perhaps be more correct to regard them in exactly the opposite light. Thus, taken at their respective critical temperatures, oxygen is liquefied by a pressure of 58 atmospheres ; while at the critical temperature of chlorine this gas requires a pressure of 84 atmospheres to reduce it to the liquid state. At 0° it is true chlorine may be liquefied by a pressure of only 6 atmospheres, but it must be remembered that 0° is 141 degrees *below* the critical temperature of this gas. Long before oxygen has been cooled 141 degrees below *its* critical temperature, which would be down to −254°, it not only passes into the liquid state without the application of any external pressure at all, but is frozen to the solid state.

Diffusion of Gases.—If a jar filled with hydrogen be placed mouth to mouth with a jar of air, the hydrogen being uppermost, it will be found that after the lapse of a few minutes some of the hydrogen will have passed into the bottom jar containing air, and some of the air will have made its way up into the hydrogen jar. The light gas hydrogen does not, as might have been supposed, remain floating upon the air, which is 14.44 times as heavy, but gradually escapes into the lower jar; and the heavier gas finds its way, in opposition to gravitation, into the upper jar. This process goes on until there is a uniform mixture of air and hydrogen in both jars, and the gases never separate again according to their densities.

This transmigration of gases will take place even through tubes of considerable length: thus, if two soda-water bottles be filled one with hydrogen and the other with oxygen, and the two bottles be connected by a piece of glass tube a metre in length, the system being held in a vertical position with the light hydrogen uppermost, it will be found after an hour or two that the two gases have become mixed. Some of the hydrogen will have descended through the long tube into the lower bottle, and in like manner a portion of the oxygen, although nearly sixteen times as heavy as hydrogen, will have travelled up into the top bottle. That the gases have so mixed may be readily shown by applying a lighted taper to the mouth of each bottle, the detonation which then takes place proving that the bottles contain a mixture of oxygen and hydrogen. This passage of one gas into another is called the *diffusion of gases.* It was observed by Graham that when the two gases were separated from each other by a thin porous septum, such, for instance, as a piece of unglazed porcelain (so-called "biscuit"), or plaster of Paris, the pressure of the gas on the two sides of the porous partition did not remain the same during the process of diffusion: that is to say, one gas made its way through the partition faster than the other, and it was noticed that the lighter the gas the more rapidly was it able to transpire or diffuse through the porous medium. This fact, viz., that a light gas diffuses more rapidly than a heavier one, may be observed in a variety of ways.* The apparatus seen in Fig. 8 is a modified form of Graham's diffusiometer. It consists of a long glass tube with an enlargement or bulb near to one end. Into the short neck of this bulb there is fastened a thin diaphragm of stucco, or other porous material. If the apparatus be filled with hydrogen by displacement, the short neck being closed by a cork, and the long limb be immersed in water, it will be seen, upon the withdrawal of the cork, that the water rapidly rises in the long tube. The hydrogen diffusing out through the diaphragm so much more rapidly than air can make its way in, a diminution in pressure within the apparatus results, and this causes the water to ascend in the tube. The same phenomenon may be seen even more strikingly by means of the apparatus, Fig. 9, which consists of a tall glass U-tube, upon the end of one limb of which there is fastened, by means of a cork, a porous cylindrical pot, such as

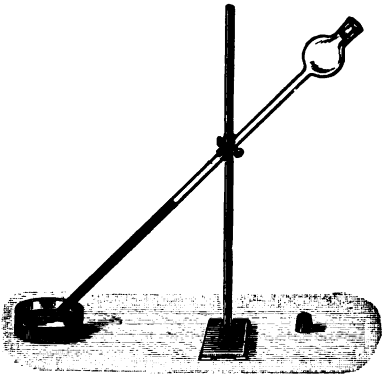

FIG. 8.

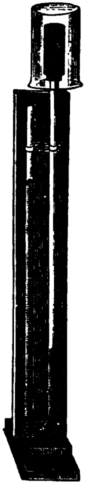

FIG. 9.

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* See Experiments Nos. 350–359, Newth's "Chemical Lecture Experiments," new ed.

is used in an ordinary Bunsen battery. The U-tube is half filled with coloured water. Under ordinary circumstances air is continually diffusing through the porous pot, but as it passes at an equal rate in both directions, there is no disturbance of the pressure, and consequently the coloured water remains level in the two limbs. If now a beaker containing hydrogen be brought over the apparatus, as seen in the figure, the hydrogen will stream through the porous pot so much more rapidly than the air in the pot can make its way out, that there will be an increase in the total amount of gas inside the apparatus, which will be instantly rendered evident by the change of level of the liquid in the U-tube, the water being forcibly driven down the tube which carries the porous pot. Upon removing the beaker the reverse operation will at once take place; the hydrogen inside the apparatus now rapidly diffuses out, and much more quickly than air can pass in, consequently a reduction of pressure within the apparatus results, which is indicated by a disturbance of the level of the water in the tube, in the opposite direction to that which occurred at first.

The Law of Gaseous Diffusion.—Graham established the law according to which the diffusion of gases is regulated, and it may be thus stated: *The relative velocities of diffusion of any two gases are inversely as the square roots of their densities.*

The density of hydrogen being 1, that of air is 14.44, the velocity of the diffusion of hydrogen, therefore, as compared with that of air, will be in the ratio of $\sqrt{14.44}$ to $\sqrt{1}$. $\sqrt{14.44} = 3.8$, $\sqrt{1} = 1$. Therefore hydrogen diffuses 3.8 times faster than air; or 3.8 volumes of hydrogen will pass out through a porous septum, while only 1 volume of air can enter.

If d = the density of a gas, air being unity, and v = the volume of the gas which diffuses in the same time as 1 volume of air, then

$$v = \sqrt{\frac{1}{d}}$$

The following table gives in the last column the results obtained by Graham, which will be seen to accord very closely with the calculated numbers demanded by the law of diffusion :—

Name of Gas.	Density of Gas compared with Air $= d$.	$\sqrt{\frac{1}{d}}$	Volume of Gas which Diffused in the same Time as one Volume of Air.
Hydrogen . . .	0.06926	3·7794	3·83
Marsh gas . . .	0.559	1·3375	1·344
Carbon monoxide . .	0.9678	1.0165	1.0149
Nitrogen	0.9713	1.0147	1.0143
Oxygen	1.1056	0.9510	0.9487
Sulphuretted hydrogen .	1.1912	0.9162	0.95
Carbon dioxide . .	1.5290	0.8087	0.812
Sulphur dioxide . .	2.247	0.6671	0.68

The property of diffusion is sometimes made use of in order to separate gases, having different densities, from gaseous mixtures. This process of separation by diffusion is known as *atmolysis*. The principle may readily be illustrated by causing a mixture of oxygen and hydrogen, in proportion to form an explosive mixture, to slowly traverse tubes made of porous material, such as ordinary tobacco pipes. Two such pipes may be arranged as shown in Fig. 10, and the gaseous mixture passed through in the direction indicated by the arrow. On collecting the issuing gas over water in a pneumatic trough, it will be found to have so far lost the hydrogen, by diffusion through the tube, that a glowing splint of wood when introduced into it will be reignited.

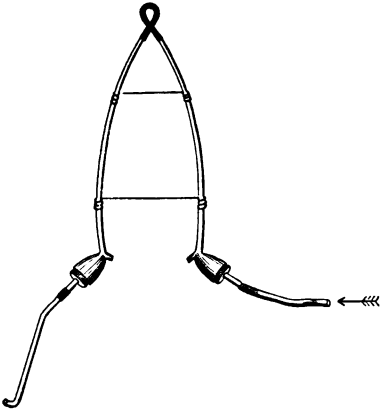

FIG. 10.

From the rate of diffusion of ozone, in a mixture of ozone and oxygen, Soret was able to calculate the density of this allotropic form of oxygen, and so confirm the result he had previously obtained by other methods (see Ozone).

Attempts have been made to utilise this principle in order to obtain oxygen from the air. The relative densities of oxygen and nitrogen are as 16 to 14; the rate of diffusion, therefore, of nitrogen is slightly greater than that of oxygen.

Effusion is the term applied by Graham to the passage of gases through a fine opening in a very thin wall, and he found that it followed the same law as diffusion. Bunsen utilised this principle for determining the density, and therefore the molecular weights, of certain gases. The method, in essence, is as follows:—A straight glass eudiometer is so constructed, that a gas contained in it can be put into communication with the outer air through a minute pin-hole in a thin platinum plate. The gas is confined in the tube, which is placed in a cylindrical mercury trough, by means of a stop-cock at the top. When the tube is depressed in the mercury, and the cock opened, the gas escapes through the minute perforation in the platinum plate, and its rate of effusion is determined by the time occupied by a glass float placed in the tube in rising a graduated distance within the eudiometer.

The flow of gases through capillary tubes is called *transpiration of gases.* In this case the friction between the gas and the tubes becomes a factor in the movement, so that this phenomenon is not governed by the same law as gaseous diffusion.

The Kinetic Theory of Gases.—The term *kinetic* signifies motion, and as applied to this theory it expresses the modern views of physicists concerning matter in the gaseous state, and serves to harmonise and explain the physical laws relating to the properties of gases. Matter in the state of gas or vapour is regarded as an aggregation of molecules in which the attractive forces which tend to hold them together are reduced to a minimum, and in which the spaces that separate them are at a maximum. These molecules are in a state of rapid motion, each one moving in a straight line until it strikes some other molecule, or rebounds from the walls of the containing vessel, when it continues its movement in another direction until it is once more diverted by another encounter. As they constantly encounter and rebound from each other, it will be evident that at any given instant some will be moving with a greater speed than others; the majority, however, will have an average velocity. In these encounters no loss of energy results so long as the temperature remains constant, but any change of temperature results in a change in the velocity of movement of the molecules, the speed being increased with increased heat. The actual volume of the molecules is very small as compared with the space occupied by the mass; the space between the molecules, therefore, in which they pass to and fro, is relatively very great. As the molecules are constantly colliding and rebounding, the distances between them, as well as their speed, will be sometimes greater and sometimes less ; but there will be an average distance, which is known as the *mean free path* of the molecule.

The pressure exerted by a gas, or its elastic force, is the combined effect of the bombardment of its molecules against the containing vessel ; in other words, the pressure of a gas is proportional to the sum of the products obtained by multiplying the mass of each molecule by half the square of its velocity. It will be obvious that if the space within which a given mass of gas is confined be reduced, the number of impacts of the molecules against the walls of the containing vessel, in a given time, will be increased, and therefore the pressure it exerts, or its elastic force, will also be increased. If the space be reduced to one-half the original, the number of these impacts will be doubled, or in other words, the number of impacts in a given time is inversely as the volume. This statement is simply the law of Boyle stated in the language of the kinetic theory.

When a given mass of gas contained in a confined space is heated, the pressure it exerts, or its elastic force, is increased. But as the number of molecules present has not been increased by raising the temperature of the gas (provided no chemical decomposition of the gas is brought about by the change of temperature), the increased pressure can only have resulted from the greater frequency, and greater energy, of the impacts of the molecules against the walls of the vessel, owing to their greater velocity.

Two equal volumes of different gases under the same conditions of temperature and pressure, exert the same elastic force upon the containing vessels, that is to say, the kinetic energy in each volume is the same. According to Avogadro's hypothesis, equal volumes of all gases under the same conditions of temperature and pressure contain an equal number of molecules, however much the weight of these molecules may vary ; therefore the average kinetic energy of each individual molecule will be the same. It follows from this that the mean velocities of different molecules must vary, and the calculated numbers representing the actual velocities of movement of the molecules of different gases show that these rates are proportional to the inverse square roots of their respective densities. But according to the law of gaseous diffusion (Graham's law), the relative rapidity of diffusion of gases is inversely proportional to the square roots of their densities, hence by purely mathematical processes, based upon the kinetic theory of gases, the law of gaseous diffusion is proved to be true. Similarly, the kinetic theory is applicable to the consideration of the phenomena of evaporation and condensation (see page 126), and to the processes of solution (page 148).

The deviations from the laws of Boyle and Charles, already referred to,* are also explained by the dynamical theory of gases, from considerations of the following order :—

1. That the molecules themselves are not mathematical points, but occupy a space ; in other words, the space occupied by the actual particles of matter is not *infinitely* small as compared with the entire volume of the gas, *i.e.* the bulk of the particle *plus* the intermolecular spaces.

While the pressure upon a gas is only slight, and therefore the total volume occupied by a given mass of the gas is great, the bulk of the actual particles themselves becomes a vanishing quantity in comparison with the total volume (*i.e.* the space occupied by particles, *plus* the intermolecular spaces), and the gas under these circumstances tends to approach more nearly to the conditions of an *ideal* gas. But when the pressure is increased, and the total volume thereby greatly reduced, then the bulk of the particles themselves begins to bear an appreciable proportion to the total volume occupied by the gas.

2. That the impact of the molecules against each other and against the containing envelope occupies time ; or, in other words, the time occupied by the impacts is not *infinitely* small compared with the time elapsing between the impacts.

3. That the molecules themselves are not entirely without attraction for each other ; that is to say, although the attractive force between the molecules which holds them together in the liquid and solid states of matter is at a minimum in the case of gases, it is not *entirely* absent.

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* See page 71.

CHAPTER X

DISSOCIATION—REVERSIBLE OR BALANCED ACTIONS

DISSOCIATION is the term employed to denote a special class of chemical decompositions. When potassium chlorate is heated it breaks up into potassium chloride and oxygen, thus—

$$2KClO_3 = 2KCl + 3O_2,$$

and when calcium carbonate (chalk) is heated it breaks up into calcium oxide (lime) and carbon dioxide—

$$CaCO_3 = CaO + CO_2.$$

In the first case the oxygen is incapable of reuniting with the potassium chloride, but in the second, the carbon dioxide can recombine with the lime and reproduce calcium carbonate : therefore both the following expressions are possible—

$$CaCO_3 = CaO + CO_2,$$

and

$$CaO + CO_2 = CaCO_3.$$

Reactions of this order are known as *reversible* or balanced actions, and the breaking up of calcium carbonate by the action of heat is termed dissociation, while that of the potassium chloride under similar circumstances is simple decomposition.

When ammonia is passed through a tube heated to a dull red heat, the gas is *decomposed* into nitrogen and hydrogen—

$$2NH_3 = N_2 + 3H_2,$$

and the two gases pass out of the heated tube as separated gases, and do not recombine again.*

But when steam is strongly heated it is *dissociated* into oxygen

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* Nitrogen and hydrogen can be caused to unite under suitable conditions (see Ammonia).

and hydrogen, and as these separated gases pass away from the heated region they reunite, forming molecules of water vapour. Such a reversible reaction may be thus expressed—

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

Again, when the gases ammonia and hydrochloric acid are brought together at the ordinary temperature, they unite to form solid ammonium chloride, and when ammonium chloride is heated it dissociates into its two generators,* hence we have the expression—

$$NH_3 + HCl \rightleftarrows NH_4Cl.$$

The corresponding compound containing phosphorus in the place of nitrogen dissociates at a temperature as low as $-20°$, hence when hydrogen phosphide and hydrochloric acid are mixed at ordinary temperatures no combination takes place, the separate molecules are in the same relation to one another as those of ammonia and hydrochloric acid at a *high* temperature. When, however, the mixture of gases is cooled below $-20°$, union takes place and crystals of phosphonium chloride are formed, which at once begin to dissociate into the original gases as the temperature again rises. The change, as before, may be represented as a reversible one—

$$PH_3 + HCl \rightleftarrows PH_4Cl.$$

In such cases of dissociation as that of calcium carbonate, where one of the products is gaseous and the other solid, no difficulty exists in separating the simpler compounds that result from the decomposition ; but where the products are entirely gaseous, special methods have to be adopted to withdraw the one from the other, while they still exist as separate molecules, and before they reunite again. One such method, which is well adapted for the qualitative illustration of dissociation, is based on the law of gaseous diffusion. If when ammonium chloride is heated it is dissociated into ammonia, NH_3, and hydrochloric acid, HCl, these two gases, having the relative densities of 8.5 and 18.25, will diffuse through a porous medium at very different rates. According to the law of diffusion, these rates will be inversely as the square roots of the densities of the gases ; if, therefore, the conditions are so arranged

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* Baker has shown (May 1894) that when *absolutely* dry, these gases do not combine ; and also, that when aqueous vapour is *entirely* absent, ammonium chloride does not undergo this dissociation.

that the heating of the ammonium chloride takes place in the neighbourhood of a porous diaphragm, more of the light ammonia gas will diffuse through in a given time than of the heavier hydrochloric acid, so that a partial separation of these gases will be effected. Fig. 11 shows a convenient arrangement for carrying out the experiment. A fragment of ammonium chloride is heated in a short glass tube through which passes the stem of an ordinary clay tobacco pipe. As the dissociation takes place, both of the gaseous products begin to diffuse into the interior of the porous clay pipe, but owing to their greater rate of diffusion, a larger number of ammonia molecules will pass in, than of hydrochloric acid, in the same time; consequently, when the gases pass away from the heated region and once more recombine, there will be a surplus of ammonia molecules within the porous pipe, and for the same reason an excess of hydrochloric acid molecules outside. If the gaseous contents of the porous tube be driven out by means of a stream of air from an ordinary bellows, the presence of the free ammonia may be recognised by allowing the air to impinge upon a piece of paper, coloured yellow with turmeric, which is instantly turned brown by ammonia. The excess of hydrochloric acid within the glass tube may also be proved by placing a piece of blue litmus paper in the tube before heating the compound, and it will be reddened by the free hydrochloric acid.

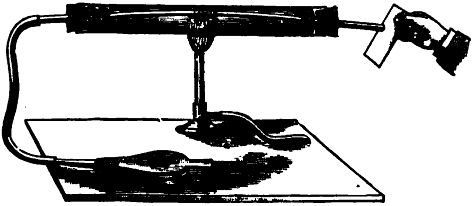

FIG. 11.

In all cases of dissociation we may imagine two opposing forces in operation, one being the external force supplying the energy which tends to bring about the disruption of the molecules, and the other being the force of the chemical affinity existing between the disunited portions of the molecule, which tends to bring about their reunion. When these forces are equally balanced, the same number of molecules are dissociated as are recombined in a given unit of time, and the system is said to be in a state of equilibrium. If by any means the balance between the two opposing forces is disturbed, by augmenting or lessening either one or the other of them, the equilibrium of the system will also be disturbed and a new condition of equilibrium will be set up, in which again an equal number of molecules undergo dissociation and combination in a given time, but in which the ratio of the number of united and disunited molecules is different from that which obtained under the former condition of equilibrium. The relation between these two forces may be most readily disturbed, by either a change of temperature or pressure. Thus, in the case of nitrogen peroxide, N_2O_4, when this gas is at a temperature of 26.7°, 20 per cent. of it is dissociated into molecules having the composition NO_2; and so long as this temperature is maintained this ratio of the weight of the dissociated molecules to the total weight of the system (known as *the fraction of dissociation*) still subsists.

When the temperature of the gas is raised to 60.2°, the state of equilibrium existing at the lower temperature is disturbed, and the system gradually assumes a new condition of equilibrium, where once more the actual number of molecules undergoing dissociation and recombination in a given unit of time is the same, but where the percentage of dissociated molecules in the gaseous mixture is now 52.04.

It might at first be supposed when such a gas is heated, and a temperature is reached at which the molecules are dissociated, that they would *all* dissociate, and that the process once begun would rapidly proceed until the decomposition was complete; instead of which, we find a definite fraction of dissociation corresponding to a particular temperature. This may be explained on the basis of the kinetic molecular theory. Let us imagine the gas nitrogen peroxide to be at a temperature below that at which dissociation begins, when all the molecules will have the composition N_2O_4. The molecules of the gas are in a state of rapid movement, and the rapidity of their movement is increased by rise of temperature. But the molecules in a given volume of the gas do not all move at the same velocity, and therefore they have not all the same temperature. On account of the infinite complications in their movements, caused by their impacts against one another, some will be moving at a speed considerably greater than that of the average, and will have a temperature proportionally higher, while others again will have a velocity and a temperature below the average.

The observed temperature of the gas, therefore, is not that of the molecules having the highest or the lowest velocity and temperature, but is the average or mean temperature between, possibly, a very wide range.

On the application of heat to the gas, the observed or mean temperature rises, but the velocity of some of the molecules, and consequently their temperature, may have been thereby raised to the point at which dissociation takes place, and they consequently separate into the simpler molecules. Let us suppose that the observed temperature of the nitrogen peroxide is 26.7°, and that it is maintained at this point. Although this temperature may be below the dissociation temperature of the molecules, it must be remembered that it only represents the *mean* temperature, and that while some of the molecules have a lower, some also have a higher temperature. As already mentioned, at the temperature of 26.7°, 20 per cent. of the molecules are dissociated; that is to say, at any given instant one-fifth of the total number of molecules reach a velocity which causes them to break down into the simpler NO_2 molecules, which themselves then take up independent movements. If, in the process of their movements, two of these disunited molecules come into contact with each other at a moment when their velocities are lower than that at which they dissociated, they at once reunite, so that at the same instant some are uniting and others are dissociating, and, the two processes going on equally, the percentage of disunited molecules at any moment is the same, although the actual molecules which are dissociated at one point of time may not be the identical ones that are in this state at another time. Let us now suppose the gas to be heated until the registered (*i.e.* the mean) temperature reaches 60.2°, and that it be maintained at this point. At this higher temperature a much larger proportion of the molecules will acquire a velocity at which they are unable to hold together, namely, 52.04 per cent.; but the remainder, amounting to nearly one-half, are still at a temperature below that at which dissociation takes place. Under these altered conditions a greater number of disunions and reunions takes place during a given interval of time, but the numbers are equal, and therefore the equilibrium exists. If once more the gas be further heated, until the indicated temperature is 140°, then it is found that the whole of the N_2O_4 molecules have dissociated into NO_2 molecules; that is to say, when the mean temperature has reached 140°, then even those molecules that are moving with the slowest speed have reached the temperature of dissociation. It will be evident that the rate at which the fraction of dissociation increases, as the temperature of a gas is gradually raised, will be greatest when the mean temperature approaches the *real* dissociation temperature of the gas, for the temperature of the greater number of the molecules will be coincident with, or very closely approximating to, that point.

The vapour density of nitrogen peroxide, if it could be ascertained when all the gaseous molecules had the composition N_2O_4, would be 46; while that of the gas, when entirely dissociated into NO_2 molecules, is 23. At temperatures between these extremes, the gas, consisting of mixtures of both molecules, will have a density lying between these figures, thus at 27.6° and 60.2° the density is 38.3 and 30.1 (see Nitrogen Peroxide, and also Phosphorus Pentachloride).

The effect of increased pressure upon a gas being to diminish the mean free path of the molecules, and thereby increase the number of molecules in a given space, the number of impacts between the molecules in a given time will be increased. If, therefore, while the nitrogen peroxide is maintained at a constant temperature, say 62.2°, the pressure be increased, the dissociated molecules, having shorter distances to travel, and making more frequent impacts in a given time, will unite more quickly than others are being disunited, and a fresh condition of equilibrium will be established for any particular pressure.

The case of phosphonium chloride already mentioned may be referred to as an illustration. This compound is completely dissociated into molecules of hydrogen phosphide, PH_3, and hydrochloric acid, below a temperature of 0°. If, while at this temperature, it be subjected to pressure, the dissociated molecules are caused to unite, and at a pressure of thirteen atmospheres the union is complete, the whole of the disunited molecules having combined to form molecules of phosphonium chloride, PH_4Cl.

If in the process of dissociation one of the products be withdrawn from the sphere of action, then the process may be carried on to completion. For example, in the case of calcium carbonate already quoted, if this substance is heated in such a manner that as fast as it dissociates, the gaseous product, namely the carbon dioxide, is allowed to escape and so pass away from the sphere of action, the change expressed by the equation

$$CaCO_3 = CaO + CO_2$$

will proceed until the whole of the carbonate has been converted into oxide. But if, on the other hand, the action is made to take place in a closed vessel, so that the carbon dioxide remains in contact with the lime, then the reverse action comes into operation, namely—

$$CaO + CO_2 = CaCO_3,$$

and a condition is arrived at in which the one action proceeds at the same rate as the other. The pressure exerted by the carbon dioxide under these circumstances is spoken of as the *dissociation pressure* of the calcium carbonate for that particular temperature.

If, now, when this condition of equilibrium is established the temperature be raised, the balance will be disturbed, and the materials will readjust themselves to a fresh condition of equilibrium at the higher temperature in which the dissociation pressure will also be greater. For any given temperature, therefore, the dissociation pressure is the only possible pressure at which a state of equilibrium can be established between carbon dioxide, calcium carbonate, and calcium oxide ; for if while the temperature is constant the pressure upon the gas were to be increased by external means and maintained at a higher point, union between the carbon dioxide and lime would proceed until the whole of the lime was converted into the carbonate. On the other hand, if the pressure were to be reduced and maintained at a lower point, then dissociation would go on until the action was complete and once more one of the three interacting substances would cease to exist.

Increasing and diminishing the pressure upon a gas is obviously synonymous with increasing and diminishing the number of molecules in a given volume. This in modern phraseology is called the *molecular concentration* of the gas, which embodies the same idea as the expression *active mass.* From the above illustration, therefore, it will be clear that there is some connection between the molecular concentration (or active mass) of the carbon dioxide and the rate of the chemical actions in question. This connection is thus formulated (Guldberg and Waage) : the rate of chemical action is proportional to the active mass (molecular concentration) of each of the reacting substances. Advantage is sometimes taken of these facts in determining the vapour-density of a substance which when heated dissociates into two gaseous constituents. For example, phosphorus pentachloride when heated dissociates into phosphorus trichloride and chlorine (see page 466), according to the equation—

$$PCl_5 \rightleftarrows PCl_3 \times Cl_2.$$

But if the active mass of either the chlorine or the trichloride be increased by adding more molecules of either one of these substances from some other source, the extent to which dissociation takes place will be proportionally diminished. Hence, by heating the pentachloride in an atmosphere of chlorine and thereby greatly increasing the molecular concentration of this gas, dissociation may be so far prevented that the density of the vapour is found to have practically the normal value for the compound PCl_5.

CHAPTER XI

ELECTROLYSIS AND ELECTROLYTIC DISSOCIATION

IF a strip of pure zinc and a strip of platinum be together dipped into a vessel containing dilute sulphuric acid, neither metal is affected by the acid, so long as the metals do not touch each other. If the ends of the strips outside the liquid be joined by means of a metal wire, the zinc gradually dissolves in the acid, and bubbles of hydrogen are disengaged from the liquid in contact with the surface of the platinum plate (which itself is otherwise unaffected by the acid), and at the same time an electric current passes through the wire. So long as the chemical action of the sulphuric acid upon the zinc proceeds, so long will the electric current continue to pass ; in other words, chemical energy will be transformed into electrical energy. If the wire be severed, the electric current can no longer pass, and the chemical action at once stops.

Such an arrangement constitutes a galvanic or voltaic element or cell, and a series of such cells forms a galvanic battery. The zinc plate, or the end of a wire that may be connected to it, is termed the negative pole of the battery, while the end of a wire attached to the platinum plate is the positive pole. Other arrangements can be employed for generating a galvanic current, but in all cases the electrical energy is derived ultimately from chemical action.

If the two poles of a battery are connected together by placing them both in contact with various different substances, it is seen that in some cases the electric current passes, and in others not. For instance, if the poles are joined by placing them both in contact with a bar of sulphur, no current passes, whereas when connected by a rod of graphite the current freely passes. Substances which behave in this respect like the sulphur are said to be non-conductors of electricity, while those that allow the current to pass are distinguished as conductors. Substances capable of conducting electricity are of two kinds, namely, those which are merely heated, and those which undergo a chemical change in consequence. All the metals, and a few of the non-metals, belong to the first of these classes; while the second includes a large number of compound substances, which are either in the liquid state or in solution in some solvent. Thus, if the poles of a battery are immersed in pure water, practically no current passes, because this liquid is a non-conductor; but if a quantity of hydrochloric acid (HCl) be dissolved in the water, the solution at once becomes a conductor, and it is seen that gas is disengaged from the liquid upon the surface of each wire. If the solution of hydrochloric acid is moderately strong, it will be found, upon examination, that the gas evolved at the negative pole is hydrogen, while that from the positive pole is chlorine: the hydrochloric acid, therefore, is separated into its elements by the passage of an electric current through its aqueous solution. Such a process of decomposition is termed *electrolysis;* and the conducting liquid is known as an *electrolyte.*

The poles or terminals that are introduced into the electrolyte are called *electrodes*, the negative electrode being termed the *cathode*, and the positive electrode the *anode.*

Liquids which do not conduct electricity, or conduct only with extreme difficulty, such as water, benzene, aqueous solutions of alcohol or of sugar, are called *non-electrolytes;* while those which are good conductors, such as aqueous solutions of hydrochloric acid or of sodium chloride, are called *electrolytes.* Other liquids range themselves between these two extremes with respect to their conductivity, but those which may be said to fall about midway are sometimes spoken of as *half-electrolytes.* These terms, strictly speaking, apply to the actual liquids or solutions; thus in the above examples it is the aqueous solution of sugar which is the non-electrolyte, and the aqueous solution of sodium chloride which is the electrolyte. For brevity, however, it is usual to apply the terms to the substance in solution, and to understand that an *aqueous solution* is meant unless another solvent is specially mentioned. Thus, when we say that sugar is a non-electrolyte, and sodium chloride an electrolyte, it is the aqueous solutions of these substances that are referred to.

In the class of electrolytes are included the strong acids, such as nitric, hydrochloric, and sulphuric acids; the strong bases, such as the hydroxides of the alkali metals, and almost *all* the class of substances known as salts, irrespective of whether the acids and bases they are composed of are electrolytes or half-electrolytes.

The half-electrolytes are the weak acids, such as acetic, tartaric, and oxalic acids, and the weak bases, as ammonium hydroxide and the hydroxides of divalent metals other than the alkaline earth metals. Non-electrolytes are substances of a neutral character such as sugar, this class including the large majority of *organic* compounds which do not happen to fall under the category of acids, bases, and salts.

In a great number of instances the electrolytic separation is accompanied by certain secondary reactions, caused by the action of the primary products of the decomposition upon either the electrolyte or the solvent ; for example, when a solution of sodium chloride ($NaCl$) is electrolysed, the primary products are sodium and chlorine, the latter appearing at the anode and the sodium making its appearance at the cathode. The sodium, however, in contact with the water in the neighbourhood of the cathode at once reacts with the liquid, with the liberation of its equivalent of hydrogen, according to the equation—

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

Similarly, in the case of hydrochloric acid, if the solution is sufficiently dilute the final products obtained by subjecting it to electrolysis are *not* hydrogen and chlorine, but hydrogen and oxygen. The *primary* products are the same as before, but under the altered condition the chlorine which is discharged at the anode acts upon the water, combining with the hydrogen, and liberating an equivalent quantity of oxygen : the two actions being expressed by the equations—

$$4HCl = 2Cl_2 + 2H_2$$
$$2Cl_2 + 2H_2O = 4HCl + O_2.$$

Again, when a dilute solution of sulphuric acid in water is electrolysed, the acid separates into the two primary products H_2 and SO_4. The hydrogen as before appears at the cathode, while the group or radical SO_4 passes to the anode, where it undergoes decomposition in contact with the water, reforming sulphuric acid, while oxygen escapes. Thus—

$$2H_2SO_4 = 2H_2 + 2SO_4$$
$$2SO_4 + 2H_2O = O_2 + 2H_2SO_4.$$

It will be observed that the final products are oxygen and hydrogen in the proportion of two volumes of hydrogen to one volume of oxygen; that is, the proportion in which they exist in water. This process is, in fact, the same as that frequently spoken of as the "electrolysis of water" (see page 207).

If instead of a solution of sulphuric acid, a solution of sodium sulphate, Na_2SO_4, is treated in the same way, this compound separates into the two primary products 2Na and SO_4; the sodium passing to the cathode and the SO_4 to the anode. The sodium in contact with the water reacts as explained above, liberating an equivalent quantity of hydrogen; while the SO_4 group, as before, gives rise to the reformation of sulphuric acid and the liberation of oxygen. The final products, therefore, are again hydrogen and oxygen in the same proportions as before; while the sulphuric acid and caustic soda reunite to form sodium sulphate.

In the same way, when an aqueous solution of copper sulphate ($CuSO_4$) is submitted to electrolysis, the primary products are copper, Cu, and the group SO_4. The copper is liberated at the cathode, and since it exerts no action upon the water, it is deposited as a metallic film upon the electrode.* The group SO_4 again passes to the anode, where it undergoes decomposition in the presence of the water, as in the former cases.

The primary products of electrolysis are termed the *ions*. Those ions that appear at the anode (positive electrode) are those which are negatively electrified, or which convey negative electricity; such as the elements fluorine, chlorine, bromine, iodine, and a number of acidic groups or radicals, such as the SO_4 group already mentioned. Inasmuch as the negative ions appear at the anode, they are called *anions*.

Those ions, such as hydrogen and the metals, which travel to the cathode (negative electrode) are those that are positively electrified, or in other words, which convey positive electricity: positive ions, therefore, are distinguished as *cations*.†

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* This is the essence of the process of electro-plating. The metal to be deposited, whether it be gold, silver, or nickel, &c., in the form of a suitable salt (usually a double cyanide) in aqueous solution, forms the electrolyte. The object to be plated is made the cathode, that is, it is suspended in the liquid and is connected to the negative electrode of a suitable battery. The anode consists of a strip of the metal to be deposited. Thus in silver plating, a strip of silver is employed, and in this way the acidic radical that is liberated at the anode dissolves the metal, and thereby prevents the weakening of the solution, which would otherwise result from the gradual deposition of silver upon the cathode.

† The student will sometimes meet with the words *cation* and *cathode* spelt *kation* and *kathode*, and in view of their Greek origin this no doubt is rigidly

Faraday's Law.—When the same quantity of electricity is passed through different electrolytes, the ratio between the quantities of the liberated products of the electrolysis is the same as that between their chemical equivalents.

Thus, if the two electrolytes, hydrochloric acid and dilute sulphuric acid, be introduced into the same electric circuit, hydrogen and chlorine are evolved in the one case and hydrogen and oxygen in the other. If the gases be all collected in separate measuring vessels, it will be seen (1) that the hydrogen and chlorine evolved from the hydrochloric acid are equal in volume; (2) that the volume of hydrogen collected from the other electrolyte is the same, while that of the oxygen is equal to only one-half this amount. Knowing the relative weights of equal volumes of these three gases to be hydrogen, oxygen, chlorine, as 1, 16, 35.5, we see that they must have been liberated in the proportions by weight of—

Hydrogen = 1 Oxygen = 8 Chlorine = 35.5.

Similarly, if the same quantity of electricity be passed through aqueous solutions of hydrochloric acid (HCl), silver nitrate ($AgNO_3$), copper sulphate ($CuSO_4$), and gold chloride ($AuCl_3$), by the time that 1 gramme of hydrogen has been liberated from the hydrochloric acid, there will be deposited upon the cathodes of the other electrolytic cells 108 grammes of silver, 31.7 grammes of copper, and 65.6 grammes of gold. These numbers, which are the electrochemical equivalents, are identical with the chemical equivalents of those elements, the chemical equivalent of an element being its atomic weight divided by its valency.

	H.	O.	Cl.	Ag.	Cu.	Au.
Atomic weights . .	1	16	35.5	108	63.5	197
Valency	1	2	1	1	2	3

Regarding the quantity of electricity required to liberate 1 gramme of hydrogen as the unit, we may say that 16 grammes of oxygen require 2 units of electricity for its liberation, 108 grammes of silver 1 unit, 63.5 grammes of copper 2 units, and 197 grammes

correct. But as it is undesirable to introduce unnecessary variations in the spelling of the same words, and as spelt with a "C" these terms have now become established in our language by use, they will be uniformly so printed in this book. Moreover, to be consistent quite a number of other terms which are always spelt with a "C" would have to be changed, such as *catalysis*, *catalytic*, *calorimeter*, *calorie*, &c., &c.

of gold 3 units; or, in other words, the number of units of electricity required to liberate a gramme-atom is identical with the number representing the valency of that atom in the particular electrolyte employed.

Some metals, such as copper, mercury, tin, &c., are capable of functioning with different degrees of valency. Thus copper is divalent in copper sulphate and in cupric chloride, but monovalent in cuprous chloride. If, therefore, 1 unit of electricity be passed through aqueous solutions of each of these copper chlorides, in the case of cupric chloride $\frac{63.5}{2} = 31.7$ grammes of copper will be deposited, while in the cuprous chloride $\frac{63.5}{1} = 63.5$ grammes are formed.

The Ionic Theory.—The modern theory now generally held, to explain the phenomena of electrolysis, is known as the theory of *electrolytic dissociation* or the *ionic theory*. The passage of electricity through conductors of the two classes above mentioned, that is, through conductors such as metals, and those which are electrolytes, may be compared with the two ways by which heat is transmitted, namely, by conduction and convection. When a bar of metal is heated at one end, the heat travels along the bar, the metal remaining stationary; but when water is contained in a tube which is heated at its lower end, the heated particles of water travel along the tube, conveying the heat to the other extremity. In a similar manner, when electricity passes through a metallic conductor, the electricity travels through, or along, the metal, which itself does not move;* but when it is passed through an electrolyte, it is conveyed or transported through the liquid by the moving ions. One set of ions charged with negative electricity travels towards the anode, while another set conveying positive electricity moves towards the cathode. In the earlier stages of the development of the present theory it was supposed that the electrolyte was only separated into its ions as the electric current was passed into it, that the electricity was the prime cause of the dissociation of the electrolyte, hence the expression *electrolytic decomposition*, still commonly used. It was believed (Grotthus) that the first effect of the current was to cause the molecules in the solution to take up positions towards each other and the electrodes which may be crudely

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* In the language of the modern theory of the atomic nature of electricity, it is the *electrons* which travel, while the metal ions remain (probably) stationary.

represented by the top line in the following diagram, where the molecules of hydrochloric acid, for example, are arranged with their electro-negative constituents all directed to the anode, and number of separate cells in a battery would be arranged. Then that a disruption of the molecules took place in which those nearest to the electrodes parted with their positive and negative ions to their respective electrodes (where they would be disengaged as free hydrogen and chlorine in the case of hydrochloric acid), while an exchange of partners between the other molecules all along the line took place, as represented in the second line, resulting in the formation of fresh molecules of the original compound. These would then immediately assume the position of those in the upper row. This theory, while affording an explanation of many of the phenomena connected with electrolysis (such as the fact that the ions are disengaged *only* at the surface of the electrodes, and not in the intervening space; that the appearance of the liberated ions takes place simultaneously at the two electrodes, however far removed from each other, &c.), was not capable of satisfying all the facts of the case. It was pointed out (Clausius) that if the electric current were the actual cause of the separation of the molecules into their constituent ions, this ought to be made manifest by the fact that the current would have to expend energy in doing the work of effecting such decomposition. But exact experiment shows that this is not the case. It is found that when an electric current passes through an electrolyte, no electric energy is absorbed in causing the dissociation of the molecules of the dissolved substance; but that the current is conducted by electrolytes with the same freedom as it is by metallic conductors. In other words, it has been shown that Ohm's law is equally applicable to electrolytes as it is to metals, namely, that the current is proportional to the electro-motive force for all values of that force.

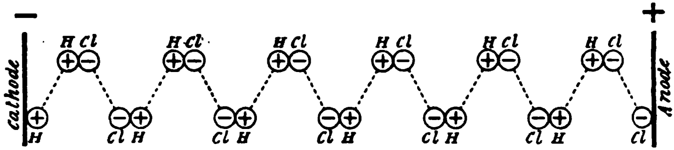

FIG. 12.

The theory of electrolytic dissociation, first proposed by Arrhenius, and now generally accepted by chemists and physicists, is that all solutions which are capable of conducting electricity contain molecules which are *already* in a state of dissociation. That is to say, the electrolyte consists of molecules which are already dissociated into their constituent ions to a greater or less extent. The simple act of solution in water results in the dissociation of a portion of the molecules into their positive and negative ions. For example, a solution of sodium chloride is an electrolyte; when, therefore, this substance is dissolved in water a certain proportion of the molecules immediately undergoes ionic dissociation, so that the solution contains some molecules of sodium chloride, some sodium ions, and some chlorine ions. In such solutions it is the *ions alone* which take any part in the conduction of the electric current, the undissociated molecules being entirely inoperative. Obviously, therefore, when a substance dissolves in water *without* undergoing ionic dissociation, the solution will be a non-electrolyte; while if dissociation only takes place to a limited extent the solution will come under the head of the half-electrolytes. Strong acids, bases, and salts, which are good electrolytes, are therefore the substances which undergo dissociation to the greatest extent. For any given solution the extent to which dissociation takes place increases as the solution is diluted until a point is reached at which all the molecules are dissociated into their ions.

At first it might appear contrary to established ideas that in such a case as sodium chloride, for instance, the sodium and chlorine in the free or separated state should be capable of existence side by side in the same liquid—a liquid, moreover, upon which one of these elements, namely, the sodium, is under ordinary circumstances capable of exerting a chemical action. Similarly, that with such a compound as sodium sulphate there should not only be the same element, sodium, existing in contact with water, but also a group of elements, or radical, SO_4, which is not known in a state of separate existence. These ions, however, whether elementary like sodium or compound like the group SO_4, are all united with and carry with them enormous electrical charges, positive or negative, as the case may be; and it is only so long as they retain their electrical charges that they can retain an independent existence and exhibit their own special properties. When the electrodes from an electric battery are introduced into a solution of sodium chloride, the sodium ions with their positive charges are attracted to the cathode; they there discharge their loads of electricity, and thereupon become ordinary molecules of sodium, possessing the properties usually associated with that metal. Hence, since ordinary sodium cannot exist in contact with water, the metal immediately upon its liberation at the cathode reacts upon the water with which it is in contact in the manner usual to sodium. Similarly, the chlorine ions with the negative electric charges are endowed with their own characteristic properties, which are retained so long as the atom is united to the electricity. So soon as it loses its charge, which it does when it conveys it to the anode, the *chloride ion* then becomes a *chlorine atom*, two of which immediately unite, forming a molecule of the element possessing the ordinary properties of chlorine gas. If, therefore, we use the term *radical* to embrace single atoms as well as groups of atoms, we may describe an ion as a radical united to an electric charge—a positive ion being one which carries positive electricity, and a negative ion being a radical which is united to a negative charge.

Indeed, instead of regarding this subject as one presenting a new difficulty to the mind, we may even trace an analogy between it and another set of ideas with which we are already quite familiar. We know that when two elements enter into chemical union with each other they lose their own characteristic properties, and that the resulting compound is endowed with new and different properties; when an atom of sodium combines with an atom of chlorine the sodium no longer exhibits the properties of metallic sodium. Similarly, when an atom of sodium is combined with a negative electric charge, the product of the union, namely, the *ion*, possesses properties differing from those of metallic sodium. The exact "how" and "why" are equally mysterious in both cases, and in neither case are we able to explain the precise nature of the union for which in both instances we employ the word "combine."

If we take as our unit the amount of electricity which is carried by one atom of hydrogen, then of all *monovalent* ions we may say that they convey one unit of electricity, for all such ions are united to equal amounts of electricity, whether they be simple or complex radicals. Divalent and trivalent ions respectively are united to two and three units of electricity. Valency may, in fact, be defined as the number of unit electric charges which are united to an atom (or radical). These electric charges are called *electrons*, or atoms of electricity, in accordance with the present-day views as to the nature of electricity. Electricity is now regarded as having an atomic structure: it is believed to consist of indivisible and indestructible particles, positive electrons and negative electrons, comparable in a measure with the atoms of monovalent chemical elements. To denote these electrons, or atomic charges of electricity, the symbols $+$ and $-$ are employed; they represent one "atom of electricity" (positive and negative respectively), just as the symbol H stands for one atom of hydrogen.*

A positive electron combined with a positive chemical atom or radical gives rise to a positive ion, or *cation;* while negative elements or radicals united to negative electrons constitute negative ions or *anions.*

In chemical notation it is usual to represent ions by employing either the ordinary $\oplus$ and $\ominus$ signs, or more commonly a dot ($\cdot$) and dash ($'$), in conjunction with the chemical symbol for the atom or radical. Thus $\overset{+}{\mathrm{Na}}$ or $\mathrm{Na}^{\cdot}$ signifies a sodium ion, and $\overset{-}{\mathrm{Cl}}$ or Cl' represents the chloride ion.

The symbol $\mathrm{Na}^{\cdot}$ therefore conveys the information that the sodium ion is a monovalent cation; while Cl' indicates that the chloride ion is a monovalent anion. SO_4'', in the same way, stands for the sulphate ion, with its two negative charges, and $\mathrm{Fe}^{\cdot\cdot\cdot}$ for the trivalent ferric ion with its triple charge of positive electricity. Sodium chloride *in solution* would be represented by the formula $\mathrm{Na}^{\cdot}\mathrm{Cl}'$, ferric chloride by $\mathrm{Fe}^{\cdot\cdot\cdot}\mathrm{Cl}'_3$, potassium sulphate by $\mathrm{K}^{\cdot}_2\mathrm{SO}_4''$, and so on.

In the system of nomenclature of the ions now generally adopted,† the names of the cations are formed by the addition of the termination *ion* to the stem of the chemical name of the element or radical; thus, hydrion, $\mathrm{H}^{\cdot}$, sodion, $\mathrm{Na}^{\cdot}$, ammonion, $\mathrm{NH}^{\cdot}_4$, calcion, $\mathrm{Ca}^{\cdot\cdot}$, zincion, $\mathrm{Zn}^{\cdot\cdot}$, &c.

When it becomes necessary to indicate the number of unit charges (*i.e.* the valency) of the radical, Greek numerals are prefixed to the name. For example, diferrion, $\mathrm{Fe}^{\cdot\cdot}$ (the ions in ferrous salts), triferrion, $\mathrm{Fe}^{\cdot\cdot\cdot}$ (the ions in ferric salts); monocuprion, $\mathrm{Cu}^{\cdot}$, and dicuprion, $\mathrm{Cu}^{\cdot\cdot}$, for the cations in cuprous and cupric compounds respectively.

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* Negative electrons are known in the free state. The "cathode" rays emitted from a Geissler vacuum tube consist of these negative electrons, and they also form a part of the "radiation" emitted by the element radium (see Appendix). So far positive electrons have not been isolated.

† First introduced by J. Walker.

In the case of anions the names are formed by the use of one of the three terminations—*idion*, *anion*, and *osion*, depending upon whether the salt radical ends in *ide*, *ate*, or *ite*. For instance, anions derived from chlor*ides*, brom*ides*, hydrox*ides*, sulph*ides*, will be chlor*idion* Cl', brom*idion* Br', hydrox*idion* OH', sulph*idion* S'' respectively; those from chlor*ates*, sulph*ates*, orthophosph*ates*, &c., chlor*anion* ClO_3', sulph*anion* SO_4'', orthophosph*anion* PO_4''', &c.; while those derived from such salts as nitr*ites* and sulph*ites* are termed nitr*osion* NO_2', sulph*osion* SO_3''. These names are employed precisely as ordinary chemical names are used, that is to say, they apply to the *material* taken collectively, and *not to the particles themselves* of which the material is composed.*

It is often convenient to regard the amount of electricity which is carried by *one gramme* of hydrogen as the unit, instead of that conveyed by one atom. The value of this unit is 96,550 coulombs. Hence these dots and dashes signify that one, two, or three times 96,550 coulombs of electricity are carried by the *gramme-molecule* (see p. 57) of the ion according to the number of these signs attached to it. Thus 96 grammes of SO_4'' will carry $96,550 \times 2$ coulombs of negative electricity; 18 grammes of $NH_4^{\cdot}$ carries $96,550 \times 1$ coulombs of positive electricity, and 95 grammes of PO_4''' conveys $96,550 \times 3$ coulombs, or 3 units of electricity. In other words, each dot and dash attached to the formula signifies one charge of 96,550 coulombs united to the gramme-molecule of the ion.

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* Just as the names sodium, hydrogen, chlorine, &c., are used to denote *matter* which is made up of atoms or molecules of sodium hydrogen or chlorine respectively, so the terms sodion, hydrion, chloridion, are the names applied to the matter which is composed of sodium ions, hydrogen ions, and chloride ions respectively. We speak of *a sodium atom*, and of *hydrogen molecules*, so also of *a sodium ion* and *hydrogen ions*. But to use such expressions as *a sodion*, or *hydrions*, is as meaningless as to speak of *a sodium* or *hydrogens*.

The translation of the chemical equation

$$2HCl = H_2 + Cl_2$$

is that hydrochloric acid is decomposed into hydrogen and chlorine—or that two molecules of hydrogen chloride yield one molecule of hydrogen and one molecule of chlorine—similarly the ionic equation

$$HCl = H^{\cdot} + Cl'$$

signifies that on solution in water hydrochloric acid is ionised into hydrion and chloridion—or that a molecule of hydrogen chloride yields on ionisation a hydrogen ion and a chloride ion.

It will be evident that *ionisation* or electrolytic dissociation is a phenomenon of a different order from that which takes place when a compound dissociates under the influence of heat, as discussed in the previous chapter. Under these circumstances it was explained that the salt ammonium chloride, for example, dissociates when heated into the two compounds NH_3 and HCl; whereas when it is dissolved in water it undergoes electrolytic dissociation into the two ions $NH_4^{\cdot}$ and Cl'; in the first case the products are electrically neutral chemical compounds, while in the latter they are electrically charged ions, or compounds of radicals with electrons.

From the point of view of the ionic theory, acid, bases, and salts all behave in a perfectly similar manner; to the "ionist," as such, there is no difference between these three kinds of substances; it is therefore sometimes convenient to class them all together as *salts*. Those which from a chemical point of view are *acids*, from the *ionic* standpoint are *salts of hydrogen*, that is, salts in which all the positive ions are hydrogen; while those which are usually termed *bases* are spoken of as *salts of hydroxyl*, or salts in which the only negative ions are hydroxide ions.*

What is understood as the *molecular conductivity* of a solution is its specific conductivity expressed in the usual electrical units, divided into the number of gramme-molecules of the dissolved substance contained in the solution; or what is the same, multiplied by the number of litres of the solution which contains one gramme-molecule of the substance.

Now since it is the ions present in an electrolyte which alone take any part in the conveyance of electricity, the undissociated molecules present being inoperative, it will be obvious that the molecular conductivity of an electrolyte will depend partly upon the number of ions present—in other words, upon the extent to which the electrolyte is dissociated—and partly upon the rate at which the ions travel or migrate in the liquid.

It has been found (Hittorf) that different ions under the same conditions travel at different rates. From determinations of the changes in concentration which take place in the electrolyte

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* The student will not fall into the error of supposing that it would be either desirable or possible to abolish the classification of acids, bases, and salts. From a purely chemical standpoint acids and bases are two perfectly distinct classes of compounds, and these two terms will always be employed to denote them.

immediately round the electrodes, it has been shown that in a solution of given concentration and under the same electrical conditions, all the ions of one kind travel with a constant velocity, but that the rate differs for different kinds of ions. For example, it is found that the ion $\mathrm{H}^{\cdot}$ migrates with a velocity about twice as great as that at which the negative ion HO' travels, and about five times the rate at which the cation $\mathrm{K}^{\cdot}$ migrates.

When, therefore, a solution is diluted, and its molecular conductivity thereby increased, this increased conductivity will be due partly to the greater rate of migration of the ions which follows upon dilution, and partly to the increased number of ions present; for, as already stated, as the solution is diluted more and more, so ionisation takes place to a greater extent.

It is found by experiment that as the solution is diluted, the molecular conductivity at first rises somewhat rapidly, that is to say, a moderate increase of dilution causes a considerable rise in conductivity; but after a certain dilution is reached, the rate of increase of molecular conductivity is greatly diminished; and after continuing slowly to increase on further dilution, a point is at length reached beyond which no increase of conductivity follows upon additional dilution. The conductivity at this latter point is called the *molecular conductivity at infinite dilution*, and at this point the whole of the electrolyte has become dissociated into its ions. The point of dilution at which the rate of increase of molecular conductivity makes the marked change may be regarded as the point at which dilution ceases to influence the rate of migration of the ions.

Since the molecular conductivity is in this way dependent upon two factors, namely, the speed of migration of the ions and the degree of ionic dissociation, it will be obvious that it cannot by itself afford a true measure of dissociation. The *dissociation coefficient*, or the fraction of the molecules of an electrolyte which are dissociated into their ions at a given concentration, is the ratio between the molecular conductivity at that concentration to the molecular conductivity at infinite dilution. Hence, if m_{∞} and m_c are the molecular conductivities at definite dilution and at concentration c respectively, then the coefficient of dissociation d will be—

$$d = m_c / m_{\infty}.$$

Some general idea of the degrees of dilution which are being dealt with in these considerations may be gained from a single example. Thus in a solution of common salt, the strength of the solution at which the rate of the migration of the ions is practically unaffected by further dilution is such that one litre contains about $\frac{1}{10}$th of a gramme-molecule of the salt, or 5.85 grammes; while a solution which has been diluted until its molecules are wholly dissociated contains only about $\frac{1}{10000}$th of a gramme-molecule per litre, or is a thousand times more dilute.

The ionic theory is in harmony with and derives support from the laws which regulate the influence of substances in solution upon osmotic pressure (page 158), upon the lowering of the vapour-pressure (page 135), and upon the lowering of the freezing-point of the solvent (page 140). Dilute solutions of electrolytes are found to exhibit deviations from these laws much in the same way that gases which undergo dissociation depart from the usual gas laws. Thus it is observed that in the case of dilute solutions of electrolytes, the osmotic pressure, the lowering of the vapour-pressure, and the lowering of the freezing-point of the solvent, instead of being proportional to the number of *molecules* of the dissolved substance, are proportional to the number of *dissociated ions.*

Again, this theory affords an explanation of the fact that the heat of neutralisation of one equivalent of strong acids and bases (in dilute solution) is practically a constant, namely, about 13,700 heat units or calories (see page 165). Now, in the neutralisation of, say, nitric acid by potassium hydroxide, according to the ionic theory these two reacting substances are in a state of dissociation in the dilute solution; moreover, the salt potassium nitrate, resulting from the interaction, will also be dissociated. The only product of the chemical action which is *not* dissociated is the water, as this compound is practically a non-electrolyte;* hence the process of neutralisation of this acid with this base resolves itself into the union of $H^{\cdot}$ ions with HO' ions to form molecules of H_2O, as may be seen by the equation

$$H^{\cdot},NO_3' + K^{\cdot},HO' = K^{\cdot},NO_3' + H_2O,$$

in which the formulæ for the dissociated molecules are written with their ions separated by a comma. It will be obvious, therefore,

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* Probably there is no such thing as an absolutely perfect non-electrolyte. In reality water itself undergoes ionic dissociation to a *very slight* extent. It has been estimated that in ten million litres of water there will be about one gramme-molecule in the ionic state.

that the final result, namely, the union of $H^{\cdot}$ with HO', will be the same if we substitute other strong acids or bases, thus—

$$H^{\cdot},Cl' + Na^{\cdot},HO' = Na^{\cdot},Cl' + H_2O,$$
$$H^{\cdot},H^{\cdot},SO_4'' + K^{\cdot},HO' = H^{\cdot},K^{\cdot},SO_4'' + H_2O.$$

Therefore the heat of neutralisation of dilute solutions of these acids and bases is in reality the heat of formation of H_2O molecules by the union of $H^{\cdot}$ ions with HO' ions.

Similarly, the ordinary "reactions" employed in chemical analysis, when considered from the standpoint of the ionic theory, become invested with a new meaning, and are often rendered more intelligible: one or two examples may be given. When the metal tin is precipitated from a solution of stannous chloride by means of metallic zinc, the following ionic equation expresses the change:—

$$Sn^{\cdot\cdot},Cl',Cl' + Zn = Sn + Zn^{\cdot\cdot},Cl',Cl'.$$

In other words, the two unit charges of positive electricity have been discharged by the tin ion, which then ceases to be an ion, but appears as ordinary metallic tin, and are transferred to the metal zinc, which then ceases to be ordinary metallic zinc, but passes into the solution as a zinc ion.

Again, the tests for iron in the ferric state are really tests for the triferrion $Fe^{\cdot\cdot\cdot}$, and tests for this metal in the ferrous condition are tests for the diferrion $Fe^{\cdot\cdot}$. But if a compound containing this metal should dissociate in such a manner as to afford neither $Fe^{\cdot\cdot\cdot}$ nor $Fe^{\cdot\cdot}$ ions, it will be evident that the usual reagents employed to detect these ions will yield no result. The salt potassium ferro-cyanide, $K_4Fe(CN)_6$, is a case in point. On solution this compound dissociates into the ions $K^{\cdot}$ and $Fe(CN)_6^{iv}$, and the iron in this solution, therefore, does not respond to the usual tests for either triferrion or diferrion.

Again, the action of ammonium chloride in preventing the precipitation of magnesium as hydroxide by ammonia, is explained by the fact that ammonium hydroxide being a comparatively weak base undergoes dissociation to only a slight extent into ammonion $NH_4^{\cdot}$ and hydroxidion OH'—to an extent far smaller than is the case with sodium and potassium hydroxides. Upon the addition of an ammonium salt of a strong acid, such as hydrochloric acid, we are throwing into the solution a large number of ammonium ions, which has the effect of causing the re-union of the hydroxide ions until practically the whole of the ammonium hydroxide present is in the undissociated state, and as there is now no hydroxidion present no magnesium hydroxide can be formed.

When no ammonium chloride is added, partial precipitation of magnesium hydroxide results—

$$\begin{gathered}Mg^{\cdot\cdot},Cl',Cl'+NH^{\cdot}_4,OH'+NH^{\cdot}_4,OH'\\ =Mg(HO)_2+NH^{\cdot}_4,Cl'+NH^{\cdot}_4,Cl'.\end{gathered}$$

But this process results in the introduction into the solution of $NH^{\cdot}_4$ ions, and equilibrium is established when these are present in sufficient quantity to prevent further production of hydroxidion by the dissociation of any more of the ammonium hydroxide.

Similarly the behaviour of many salts in yielding, when dissolved in water, solutions which are either acid or alkaline, admits of an ionic explanation. Sodium nitrite may serve as an example.

Unlike sodium nitrate, which yields a neutral solution, this salt when dissolved in water gives a solution which is alkaline, that is, a solution containing hydroxidion. When dissolved, the salt is first largely ionised into sodion and nitrosion,

$$NaNO_2=Na^{\cdot},NO_2''.$$

Besides these ions, however, there are also present minute quantities of hydrion $H^{\cdot}$ and hydroxidion OH' due to the very slight ionisation of the water itself, hence we have the ions

$$Na^{\cdot}+NO_2'+H^{\cdot}+OH'.$$

Since nitrous acid is a weak acid, *i.e.* one which is only slightly ionised in solution, the NO_2' and the $H^{\cdot}$ ions tend to unite to form molecules of undissociated nitrous acid, HNO_2, thereby causing more water molecules to become ionised, with the consequent increase in the number of hydroxide ions present. This process goes on until equilibrium is established, which may be thus represented—

$$Na^{\cdot}+HNO_2+OH'.$$

Sodium hydroxide being a strong base, the hydroxidion and sodion do not unite to form molecules, but remain in the ionic state.

Processes of this order are spoken of as *hydrolysis*—the sodium nitrite in this case is said to be *hydrolysed*. All salts of weak acids with strong bases behave in a similar manner.

CHAPTER XII

CLASSIFICATION OF THE ELEMENTS

It has already been mentioned (page 7), that the elements may be classified under the two subdivisions, *metals* and *non-metals.* Further classifications have from time to time been in use, based upon other properties, such, for example, as the valency of the elements.

Classified according to their valency, the elements fall into six subdivisions, consisting of mono-, di-, tri-, tetra-, penta-, and hexavalent elements. This system of classification has now largely fallen into disuse, owing partly to the difficulties arising out of the variability of valency so often exhibited, but more especially to the more recent development of another system, known as the *natural classification of the elements*, or the *periodic system*, which practically absorbs and includes the older method.

Certain remarkable numerical relations have long been observed to exist among the atomic weights of elements that closely resemble one another in their chemical habits. In such groups or families it is frequently seen that the atomic weight of one member is approximately the arithmetic mean of the atomic weights of those immediately before and after it, when they are arranged in order of their atomic weights. This will be seen from the following examples :—

Li.	Na.	K.	
7	23	39	$\frac{7+39}{2} = 23$
K.	Rb.	Cs.	
39	85	133	$\frac{39+133}{2} = 85.8$
P.	As.	Sb.	
31	75	120	$\frac{31+120}{2} = 75.5$
S.	Se.	Te.	
32	77	125	$\frac{32+125}{2} = 78.5$

If the elements in these various families are so arranged, as to bring out the differences between their atomic weights, the striking fact will be observed that the increase in the atomic weights in each group takes place by practically the same increment. In the following table the elements belonging to the same group are placed in vertical columns, the differences between the various atomic weights being placed between them :—

F = 19	N = 14	O = 16	Na = 23	Mg = 24
Difference . 16.5	Diff. . 17	Diff. . 16	Diff. . 16	Diff. . 16
Cl = 35.5	P = 31	S = 32	K = 39	Ca = 40
Difference . 44.5	Diff. . 44	Diff. . 47	Diff. . 46.2	Diff. . 47.3
Br = 80	As = 75	Se = 79	Rb = 85.2	Sr = 87.3
Difference . 47	Diff. . 45	Diff. . 46	Diff. . 47.8	Diff. . 49.7
I = 127	Sb = 120	Te = 125	Cs = 133	Ba = 137

It will be seen that in each group the difference between the first and second number is about 16, while between all the others the increase in weight takes place by a number which approximates to 16 × 3.

This numerical relation between the atomic weights of elements of the same family, and between the various groups, is obviously not a chance one, and chemists were led by it to believe that the properties of the elements were in some way related to their atomic weights. Newlands (1864) was the first to point out, that if the elements are tabulated in the order of increasing atomic weights, the properties belonging to each of the first seven elements reappeared in the second seven, and he applied to this relation the name of *the law of octaves.* A more elaborated and systematic representation of Newlands' law of octaves was afterwards developed by Mendelejeff (1869), and which is now generally known as Mendelejeff's periodic law. At the present time, owing to the recent discovery of the argon family of elements, it is not until *eight* elements have been traversed that the properties of the first reappear; the term "octaves" is therefore no longer strictly applicable.*

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* Unless, indeed, we stretch the musical simile somewhat and look upon these five inert gases as "accidentals."

If the sixteen elements with lowest atomic weights, after hydrogen, be arranged in order of increasing atomic weights in two horizontal rows of eight, some of these relations will be recognised—

He=4 Li=7 Be=9 B=11 C=12 N=14 O=16 F=19.
Ne=20 Na=23 Mg=24 Al=27 Si=28 P=31 S=32 Cl=35.5.

In traversing the upper row from helium to fluorine, we meet with certain characteristic properties belonging to each member, and also a certain gradation in those properties that are common. Coming to the second row, many of the characteristic properties of the members of the first row again appear, and the same regular modulation is met with in passing along the series: thus helium exhibits a likeness to neon, lithium resembles sodium, carbon corresponds to silicon, fluorine to chlorine, and so on. These resemblances are seen both in the physical as well as the chemical properties of the elements, thus lithium and sodium are both soft white metals, and are strongly electro-positive. Fluorine and chlorine are both pungent corrosive gases, and are intensely electro-negative; while helium and neon are neither electro-positive nor electro-negative, have no chemical properties whatever, and therefore no valency. Taking their power of combining with chlorine and with hydrogen as indicative of their valency, we see that the change in this respect, as the two series are traversed, is the same in each, thus—

$$\begin{array}{llllllll} \text{LiCl} & \text{BeCl}_2 & \text{BCl}_3 & \overbrace{\text{CCl}_4 \quad \text{CH}_4} & & \text{NH}_3 & \text{OH}_2 & \text{FH.} \\ \text{NaCl} & \text{MgCl}_2 & (\text{AlCl}_3)_2 & \text{SiCl}_4 \quad \text{SiH}_4 & & \text{PH}_3 & \text{SH}_2 & \text{ClH.} \end{array}$$

The gradation in properties exhibited by the elements in a series is also seen in their power of combining with oxygen, which will be more clearly brought out if the formulæ of the compounds be so written as to indicate the relative proportions of oxygen with which two atoms of each element unite, thus—

$$\begin{array}{ccccccc} \text{Na}_2\text{O}\,* & (\text{Mg}_2\text{O}_2) & \text{Al}_2\text{O}_3 & (\text{Si}_2\text{O}_4) & \text{P}_2\text{O}_5 & (\text{S}_2\text{O}_6) & \text{Cl}_2\text{O}_7 \\ & \text{MgO} & & \text{SiO}_2 & & \text{SO}_3 & \end{array}$$

Regarding, then, the eight elements of the first row as a *period*, we find that the various properties exhibited by the several members are met with again in those of the second period.

* See footnote on page 529.

Not only do the properties of the elements themselves reappear, but also those possessed by the various compounds they form: thus lithium chloride (LiCl) and sodium chloride (NaCl) strongly resemble one another. The oxides of beryllium and magnesium (BeO and MgO) have similar properties. The compounds of fluorine and chlorine with hydrogen (HF and HCl) closely resemble each other, and so on.

This periodic reappearance of similar properties, exhibited by the elements and their compounds as the atomic weights of the former gradually increase, is thus stated by Mendelejeff in his law of periodicity. *The properties of the elements, as well as the properties of their compounds, form a periodic function of the atomic weights of the elements.*

When the tabulation of the elements according to this system is continued (after the completion of the second period with chlorine), it will be seen that, beginning with argon, eighteen elements have to be arranged before we meet with the reappearance of those properties that belong to the first; that is to say, there are two "octaves," one containing eight members like the former ones, and one containing seven, and three elements over, which in the following table are placed within brackets :—

A.[*]	K.	Ca.	Sc.	Ti.	V.	Cr.	Mn.	(Fe.	Co.	Ni.)
40	39	40	44	48	51	52	55	(56	59	59)
		Cu.	Zn.	Ga.	Ge.	As.	Se.	Br.		
		63.5	65	70	72	75	79	80		

This constitutes what is known as a *long period*, in contradistinction to the two first, which are distinguished as short periods. In certain respects, however, the last seven elements in this long period exhibit resemblances to the seven in the first portion (counting after the first element, argon); that is to say, the properties displayed by the members of the first period, which is known as the *typical period*, reappear twice over in the long period. The three elements within the brackets are termed by Mendelejeff *transitional elements.* Continuing the arrangement from bromine, another long period occurs, again containing three transitional elements :—

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[*] It will be noticed that the element argon, A, is placed before potassium, K, although, according to the atomic weights here given, it would appear as though they should be in the reverse order. This will be discussed later.

Kr.	Rb.	Sr.	Y.	Zr.	Nb.	Mo.	—	(Ru.	Rh.	Pd.)
82	85	87.6	89	90.7	94	96	?	(101.7	103	106)

Ag.	Cd.	In.	Sn.	Sb.	Te.	I.
108	112	114	118	120	125?	127

It will be seen that a gap is left where the eighth member of the first part of this period should be, an element which would correspond, in this period, with manganese in the period above. This element is at present unknown. The remaining elements belong to three other long periods, in which, however, the number of gaps is very considerable, thus—

X.	Cs.	Ba.	La.	Ce.	—	—	—	(—	—	—)
120	133	137	138	140						

—	—	—	—	—	—	—

—	—	Yb.	—	Ta.	W.	—	(Os.	Ir.	Pt.)	
		173		183	184		(191	193	195)	

Au.	Hg.	Tl.	Pb.	Bi.	—	—
197	200	204	207	207.5		

—	—	—	Th.	—	Ur.	—	(—	—	—)
			232		239.5				

—	—	—	—	—	—	—

Those elements that fall in the first eight places of the long periods are termed the *even series*, while the last seven are distinguished as the *odd series;* arranging them, therefore, in such a manner as to bring the odd and even series into columns, we get the table on page 118.

In this manner the elements are arranged in nine groups. The first of these groups contains the so-called "inert gases"—the five new elements of recent discovery, which take their place rather outside this classification scheme, regarding it from a purely chemical standpoint. And as the system of numbering the groups of elements in this periodic arrangement has become familiarised by long use, this group containing the "inert gases" has been numbered Group O, and the systematic numbering of the other groups begins as usual. The last group contains the transitional elements that come between the even and odd series of the long periods.

In each of the remaining seven groups, the elements belonging to the even series of their respective long periods, are placed to the left, while those belonging to the odd series are arranged on the right-hand side of each vertical column. In this way the groups are divided into the subdivisions A and B, in which the resemblance between the members is most pronounced. Thus in Group II., although there are certain properties common to all the members, there is a much closer similarity existing between the elements calcium, strontium, and barium than between zinc and calcium, or cadmium and barium.* The elements in the two short periods have been placed in that subdivision or family with the members of which they exhibit the closest resemblance. Thus, in Group I. lithium and sodium are more allied to potassium, rubidium, and caesium, than to copper, silver, and gold; while in Group VII. fluorine and chlorine are placed in the same family with bromine and iodine, with which they exhibit a close similarity.

In the eighth group, containing the transitional elements, the families consist of the horizontal and not the vertical rows; that is to say, the closest resemblance is between the three transitional elements in each series, elements whose atomic weights, instead of exhibiting a regular increase, as in the other families, have almost the same value, such as Fe = 56; Co = 59; Ni = 59.

A glance at the table shows that in the last three long periods there is a large number of gaps. It is possible that these gaps may represent elements which yet await discovery. This supposition gains considerable support from the fact, that at the time Mendelejeff first formulated the periodic law, there were three such gaps in the first long period, which have since been filled up by the subsequent discovery of three new elements; these will be referred to later.

The periodic recurrence of some of the chemical properties is indicated in the lowest horizontal column, where the general formulæ of the oxygen compounds and the hydrides are given; R standing for one atom of any element in the group. As explained on page 114, these formulæ are so written as to show the relative amount of oxygen to two atoms of element, in order to establish the true relation between the different groups. For example, the

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* This, however, is by no means uniformly the case; thus the element copper (Group I.) in many of its chemical attributes is much more closely allied to mercury (Group II.) than to silver; and silver, again, more strongly resembles thallium (Group III.) than either copper or gold, with which it is associated in this system of classification.

	Group 0, the Inert Gases.	Group I.		Group II.		Group III.		Group IV.		Group V.		Group VI.		Group VII.		Group VIII.
		A	B	A	B	A	B	A	B	A	B	A	B	A	B	
1st short, or typical, period	He	(H)? Li		Be	—	—	B	—	C	—	N	—	O	(H)?	F	
2nd short period	Ne	Na		Mg			Al		Si		P		S		Cl	
1st long period even series	A	K		Ca		Sc		Ti		V		Cr		Mn		Fe, Co, Ni
1st long period odd ,,			Cu		Zn		Ga		Ge		As		Se		Br	
2nd long period even series	Kr	Rb		Sr		Y		Zr		Nb		Mo		—		Ru, Rh, Pd
2nd long period odd ,,			Ag		Cd		In		Sn		Sb		Te		I	
3rd long period even series	X	Cs		Ba		La		Ce		—		—		—		— — —
3rd long period odd ,,			—		—		—		—		—		—		—	
4th long period even series		—		—		Yb		—		Ta		W		—		Os, Ir, Pt
4th long period odd ,,			Au		Hg		Tl		Pb		Bi		—		—	
5th long period even series		—		—		Th		—		—		U		—		— — —
5th long period odd ,,			—		—		—		—		—		—		—	
Oxygen compounds . . .	—	R_2O		R_2O_2		R_2O_3		R_2O_4		R_2O_5		R_2O_6		R_2O_7		(R_2O_8)
Hydrogen compounds . .	—	—		—		—		RH_4		RH_3		RH_2		RH		

oxides of the elements of Group I. contain two atoms of the element to one of oxygen, as Li_2O; but those of the second group only contain one atom of the element, as CaO: hence the general formula is doubled, R_2O_2. It will be seen, therefore, that the proportion of oxygen relative to two atoms of the element regularly increases from the first group to the eighth. The oxides of the members of Group I. are strongly basic in character, and in general this basic nature gradually diminishes as we traverse the series, giving place to acidic characteristics, which are strongly marked in the seventh group.

The periodic reappearance of the physical properties of the elements is seen in such points as their electrical characters, their malleability, ductility, melting-points, &c., all of which are in harmony with the periodic law; but in none is it more strikingly seen than in their atomic volumes in the solid state. The atomic volumes of the elements are the relative volumes occupied by quantities proportional to their atomic weights, or by gramme-atoms; and they are obtained by dividing the atomic weights of the elements by their specific gravities. In the case of gases, as has been already explained on page 40, the specific gravity is the density referred to hydrogen as the unit: the atomic volume, therefore, of such a gas as oxygen is—

$$\frac{16 = \text{atomic weight}}{16 = \text{density}} = 1.$$

The specific gravities of solids (and also liquids) are referred to water as the unit, and as 1 cubic centimetre of water weighs 1 gramme, the specific gravity of a solid or liquid expresses the weight in grammes of 1 cubic centimetre of the substance. Dividing the atomic weight, expressed in grammes, by the weight in grammes of 1 cubic centimetre (*i.e.* the specific gravity), the atomic volume will be represented in cubic centimetres. It must be remembered that the atomic volumes do not express the relative volumes that are actually occupied by the atoms, they represent in reality the relative volume of the atoms *plus* the unknown volumes of the spaces that separate them.

The following table gives the specific gravities and the calculated atomic volumes of the first and the middle elements of the two short and two long periods, not counting the group of "inert" elements:—

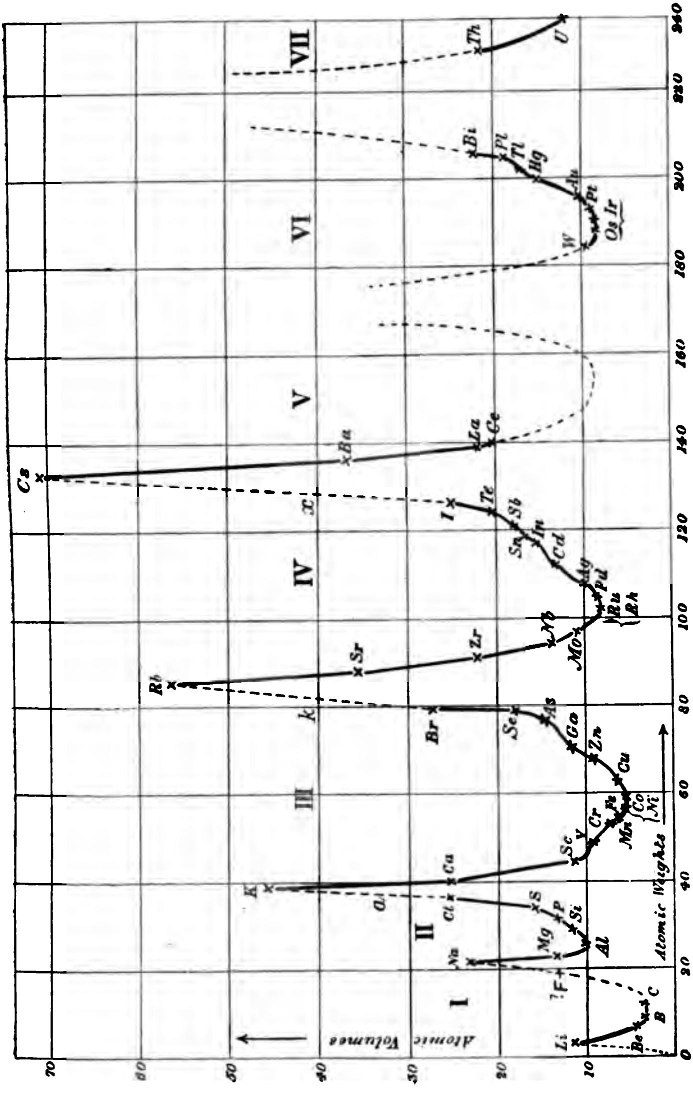
		Specific Gravity.	Atomic Weights.	Atomic Volumes.
1st Period	Lithium.	0.59	7	11.9
	Carbon.	3.0	12	4
2nd Period	Sodium.	0.97	23	23.6
	Silicon.	2.4	28.3	11.8
3rd Period	Potassium	0.865	39	45
	Iron (Cobalt-Nickel)	7.79	56	7.2
4th Period	Rubidium	1.52	85	56.0
	(Ruthenium-Rhodium) Palladium.	11.4	106.2	9
	Caesium	1.88	133	70

From the figures in the last column it will be seen, that beginning with lithium, 11.9, the atomic volume falls as the middle element of the period, namely, carbon, is reached; after which it again rises and reaches a maximum with the first member of the second period, namely, sodium. In this period the same gradual fall in atomic volume is again noticed until the middle element (silicon) is reached, when the value of this function of the elements once more rises, and a second maximum is attained with the first member (potassium) of the third period. The two next are long periods, and the atomic volumes steadily decrease until the middle three (transitional) elements, after which they gradually increase again to a maximum in rubidium, the starting-point of the fourth period. In the fourth period the same thing once more occurs, the minimum atomic volumes being those of the middle or transition elements, after which a maximum is again reached in caesium.

This periodicity of the atomic volumes may be graphically represented by a curve, where the ordinates represent atomic volumes and the abscissæ atomic weights. This curve, which was first constructed by Lothar Meyer, is known as Lothar Meyer's curve (page 121), and a comparison of it with Mendelejeff's table is most instructive.

The divisions indicated by the Roman numerals correspond to the different periods: Groups I. and II. being the two short periods, III. and IV. the two complete long periods, while V., VI., and VII. correspond to the fragmentary portions of the last three periods.

The transitional elements of periods III., IV., and VI. are all to be found at the minima of the large hollows; separating the even series (situated on the descending portion of the curve) from the odd series which lie on the ascending slope. The elements belong-


Atomic Volumes
Atomic Weights
0
20
40
60
80
100
120
140
160
180
200
220
240
10
20
30
40
50
60
70
I
II
III
IV
V
VI
VII
Li
Be
B
C
F
Na
Mg
Al
Si
P
S
Cl
A
K
Ca
Sc
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
As
Se
Br
k
Rb
Sr
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
x
Cs
Ba
La
Ce
W
Os Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

ing to the different groups in Mendelejeff's table are seen to occupy the same relative positions upon the different portions of this curve.

Thus in Group I. the elements Li, Na, K, Rb, Cs, are all found upon the maxima of the curve, and Cu, Ag, and Au at those points at the minima where the electro-negative properties reappear. The halogen elements (chlorine, bromine, iodine) are seen in similar positions upon the ascending, and the alkaline earths (beryllium, magnesium, calcium, strontium, barium) on the descending portions.

When the periodic law was first formulated by Mendelejeff (1869), there were a number of instances in which the system did not harmonise with the then accepted atomic weights of the elements. The discoverer boldly asserted that the atomic weights, and not the system, were at fault, and in almost every such case the careful reinvestigation of the atomic weights by numerous chemists has proved the correctness of the assertion. One or two instances may be quoted. The element indium had assigned to it the atomic weight 76. Its combining proportion is 38, and being regarded as a divalent element, its oxide was believed to have the formula InO. Having an atomic weight = 76, indium would occupy a place between As = 75 and Se = 79; but in the system (see table on page 118) there is no room for an element with such an atomic weight; and, moreover, if indium be a divalent element having this atomic weight, it should come between Zn = 65 and Sr = 87 in Group II., where again there is no room. Mendelejeff made the assumption that the oxide of indium had the formula In_2O_3, believing the element to be an analogue of aluminium (Group III.). If this be the true composition of the oxide, the atomic weight of the element would be 38 × 3 = 114, and indium would then take its place in Group III., between the elements cadmium = 112 and Sn = 118, in the odd series of the second long period. Bunsen afterwards determined the specific heat of indium by means of his ice calorimeter, and found it to be 0.057 :—

$$\frac{\text{Mean atomic heat} \quad 6.4}{\text{Specific heat} \quad . \quad . \quad 0.057} = 112.3 = \text{atomic weight (see page 48).}$$

Hence 114 and not 76 is the accepted (approximate) atomic weight of indium.

Again, the element beryllium (formerly known as glucinum) has a combining proportion of 4.6. Its chloride was believed to have the composition $BeCl_3$, and its oxide to be a sesquioxide having the formula Be_2O_3. The atomic weight assigned to the element, therefore, was 13.8.

With this atomic weight beryllium would take its place between carbon = 12 and nitrogen = 14; but according to the periodic classification there is no room for such an element, and, moreover, in such a position it would be among elements with which it has no properties in common. On the supposition that the oxide of beryllium has the formula BeO, that is, that the element is divalent, its atomic weight would have to be lowered from 13.8 to 9.1 in order to maintain the same ratio between the weights of metal and oxygen in the compound. On this assumption, beryllium would fall into the second place in the first series, between lithium = 7 and boron = 11, and in the same group as magnesium and zinc.

When the specific heat of beryllium was determined, it gave the value 0.45, and this number divided into the atomic heat constant, 6.4, gave 14 as the atomic weight. In spite of this evidence in favour of the higher value as the atomic weight of beryllium, Mendelejeff still regarded the lower number as correct, and it was suggested that possibly beryllium, like carbon and boron (elements also of very low atomic weight), had an abnormally low specific heat at ordinary temperatures. This was found to be the case (see page 48), and at 500° the specific heat of beryllium was found to be 0.6206. This divided into 6.4 gives the value 10 as the atomic weight, which indicates that 9.1 and not 13.8 is in reality the atomic weight of beryllium.

Not only has the periodic law been of service in bringing about the correction of a number of doubtful atomic weights, but by means of it its originator was enabled to predict with considerable certainty the existence of hitherto undiscovered elements, and even to predicate many of the properties of these elements. As already mentioned, at the time when the periodic law was first formulated, there were three gaps in the system in the first long period, namely, No. 4 in the even series (now occupied by scandium), and Nos. 3 and 4 in the odd series (now filled by gallium and germanium). To the unknown elements which were destined to occupy these positions, Mendelejeff gave the names *eka-boron*, *eka-aluminium*, and *eka-silicon* (the prefix eka being the Sanscrit numeral *one*), and from the known properties of the neighbouring elements of the series (horizontal rows in the table, page 118), and also of those situated nearest in the same family (vertical columns), he predicted some of the prominent properties that would probably be possessed by these elements. Thus in the case of eka-aluminium, from the known properties of aluminium and indium, the neighbouring elements in the same family, and from zinc, the contiguous element in the same series (the 4th place in the series being unoccupied), Mendelejeff deduced the following properties for the unknown element that he called eka-aluminium :—

PREDICTED PROPERTIES OF EKA-ALUMINIUM (1871).

(1.) Should have an atomic weight about 69.
(2.) Will have a low melting-point.
(3.) Its specific gravity should be about 5.9.
(4.) Will not be acted upon by the air.
(5.) Will decompose water at a red heat.
(6.) Will give an oxide El_2O_3, a chloride El_2Cl_6, and sulphate $El_2(SO_4)_3$.
(7.) Will form a potassium alum, which will probably be more soluble and less easily crystallisable than the corresponding aluminium alum.
(8.) The oxide should be more easily reducible to the metal than alumina. The metal will probably be more volatile than aluminium, and therefore its discovery by means of the spectroscope may be expected.

In the year 1875 Lecoq de Boisbaudran discovered a new element in a certain specimen of zinc blende (zinc sulphide), the individuality of which he first recognised by the spectroscope, the spectrum being characterised by a brilliant violet line. This element he named *gallium*. The properties of this metal, as they were subsequently observed, showed that it was, in fact, the predicted eka-aluminium of Mendelejeff, as will at once be seen by a comparison of the following facts.

PROPERTIES OF GALLIUM (*discovered* 1875).

(1.) Atomic weight = 69.9.
(2.) Melting-point, 30.15°.
(3.) Specific gravity, 5.93.
(4.) Only slightly oxidised at a red heat.
(5.) Decomposes water at high temperatures.
(6.) Gallium oxide, Ga_2O_3. Gallium chloride, Ga_2Cl_6. Gallium sulphate, $Ga_2(SO_4)_3$.
(7.) Forms a well-defined alum.
(8.) Is easily obtained by the electrolysis of alkaline solutions.

In a similar manner the properties of *eka-boron* and *eka-silicon* were predicted, and the subsequent discovery of *scandium* (Nilson, 1879), and *germanium* (Winkler, 1886), whose properties were found to closely accord with these hypothetical elements, formed an additional demonstration of the truth of the periodic law.

There are at present two elements, however, which appear not to conform strictly to this periodic classification. These are the elements argon and tellurium. The atomic weight of argon according to most recent determination is 39.92, while that of potassium is 39.15. Now the periodic system requires that the atomic weight of argon shall be *below* and not *above* that of potassium. Again, the latest determinations of the atomic weight of tellurium give 127.6, as against 126.85 for iodine; while in order to conform to the periodic system the atomic weight of tellurium should be *below* that of iodine. Whether these two cases will prove to be true exceptions, or whether future investigations will show that the atomic weights here given are not the true ones, time alone will show. It must be borne in mind, however, that both argon and tellurium are elements which it is extremely difficult to obtain in a state of absolute purity, and there is considerable probability that in the latter case the element in a pure state has never yet been obtained.

The position which should be given to hydrogen in the periodic system has been the subject of much discussion. It will be noticed that in the table it is placed with a query in Group I. and again in Group VII.; its univalent character suiting either position equally well. The chief argument in favour of placing it in Group I. is its *electro-positive* character, in which it strongly resembles the elements lithium, sodium, potassium, &c., metals which may be substituted for hydrogen atom for atom; the "salts of hydrogen" (i.e. *acids*), and the metallic salts resembling each other when regarded from the ionic standpoint.

The arguments in favour of assigning it a position at the head of Group VII. are more numerous, and may be briefly summarised as follows :*—

1. Its gaseous character and low boiling-point.
2. Absence of any metallic properties.
3. The diatomic nature of its molecules H_2 (while many of the alkali metals are monatomic).
4. Readiness with which H is substituted by Cl, Br, or I, in organic compounds.
5. If placed in Group I. a series of six blank spaces is left, for as many unknown elements, whose atomic weights must all fall between $H=1$ and $He=3.96$.
6. The numerical difference between $H=1$ and $F=19$ is 18 units, which is much closer to the average of about 16 units than that between $H=1$ and $Li=7$, which is only 6 units.

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* Masson, *Chem. News*, vol. lxxiii. p. 283.

CHAPTER XIII

GENERAL PROPERTIES OF LIQUIDS

UNDER this head the following subjects will be considered:—

1. The passage of liquids into vapours or gases.
2. The passage of liquids into solids.
3. Solution.

1. The Passage of Liquids into Gases. Evaporation and Boiling.—Just as in the gaseous condition, so in the liquid state, the molecules are in a state of motion: in the liquid state, however, the mean kinetic energy of the molecules is unable to overcome the force of their mutual attraction. Some of the molecules have a smaller kinetic energy (that is, a lower temperature), and others a greater kinetic energy, than the average; and when in the course of their movements the latter strike the surface of the liquid and break through it, they continue their movements in the space above, as gaseous molecules. If the space into which they wander be unlimited, that is, if the liquid be freely exposed to the air, these molecules escape away altogether, and consequently the liquid diminishes in quantity. This process is known as *evaporation*, and as the molecules which so leave the liquid are those having the highest temperature, it follows that the temperature of the liquid, which is the average temperature of the molecules, will fall. The more completely the molecules that so escape from the surface of a liquid are prevented from falling back, that is, the more rapidly they are swept away from the immediate neighbourhood of the liquid, the more quickly will this escape of molecules take place, and therefore the greater will be the fall of temperature that results from evaporation. Thus, if a quantity of liquid, say water, be exposed in a dish so that a current of air is blown across the surface, the rate of evaporation is increased, and the temperature consequently falls lower than if the water be merely placed in a still atmosphere; similarly, if the water be placed in a vacuum the rate of evaporation is increased, because the molecules that escape from the surface of the liquid are not impeded in their motions by collisions with the molecules of air.

This fall of temperature resulting from evaporation may be readily seen by enveloping the bulb of a thermometer in a piece of thin muslin, and moistening it with water. If such a thermometer be placed by the side of a naked thermometer, it will be seen that the mercury will fall lower in the one that is moistened, and the difference will be still more marked if the instruments are placed in a draught. whereby the evaporation of the water from the muslin is accelerated.

If the space above the liquid be limited, molecules still continue to escape from the surface; but a state of equilibrium is soon established, when as many are thrown back again by rebounding from one another and from the walls of the containing vessel as leave the surface in a given time. Under these conditions the enclosed space is said to be *saturated with the vapour of the liquid.* The number of molecules which escape from the surface depends upon the temperature, and is independent of the pressure, for if the volume of a saturated vapour be forcibly diminished, it merely results in the condensation of a portion of the vapour; and if expanded, a corresponding vaporisation of an additional quantity of the liquid, the pressure remaining always constant. The number of molecules that re-enter the liquid is determined by the number and the velocity of those that exist as gaseous molecules in a unit volume. But the pressure exerted by a gas is caused by the number and velocity of the molecules in a given volume, hence

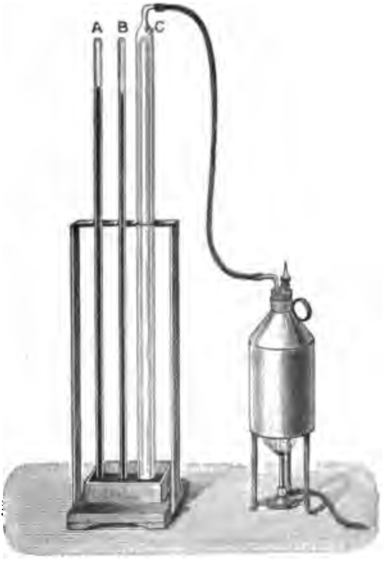

FIG. 13.

the condition of equilibrium is set up, when the vapour above the liquid exerts a definite pressure, which pressure will be constant for any given temperature. The pressure exerted by a vapour under these conditions is termed the *vapour-tension* of the liquid. The fact that the vapour given off from a liquid exerts pressure may readily be experimentally illustrated by means of the apparatus seen in Fig. 13. Three glass tubes, A, B, and C, about one metre long, are completely filled with mercury and inverted in a trough of the same liquid. The mercury will sink to the same level in each tube, the length of the mercury column representing the atmospheric pressure at the time. Into two of these barometer tubes, B and C, a few drops of water are introduced, when it will be found that the mercury is depressed, as indicated in B, below the level at which it previously stood. This depression of the mercury column represents the tension of the vapour of the water for the particular temperature at which the experiment is made. If tube C be surrounded by a wider glass tube, through which steam from a small boiler is passed, it will be noticed that as the temperature of the water in the tube rises, the mercury is more and more depressed, thus showing that the tension of the vapour increases with rise of temperature. As soon as the steam circulates freely and is escaping at the bottom of the wide tube, in other words, as soon as the temperature of the enclosed water in tube C reaches 100°, *i.e.* the temperature of the steam surrounding it, the mercury in the tube will be depressed to the level of that in the trough. The tension of the vapour within the tube, under these circumstances, is therefore equal to the atmospheric pressure.

If, instead of introducing water into the barometer tube, ether were employed, and a stream of vapour from boiling ether were passed through the outer tube, it would be seen that when the ether within the tube reached the temperature of the vapour from the boiling ether, namely, 35°, the mercury would again be depressed to the level of that in the trough; that is, the tension of the ether vapour would then be equal to the pressure of the atmosphere. We see, therefore, that when water is heated to its boiling-point, viz., 100°, the tension of its vapour is equal to the atmospheric pressure; and when ether is heated to *its* boiling-point, viz., 35°, the pressure exerted by *its* vapour is equal to the pressure of the atmosphere. The boiling-point of a liquid may therefore be defined as *the temperature at which the vapour-pressure is equal to the pressure of the atmosphere.* As soon as this point is passed, the kinetic energy of the molecules has been so much augmented by the supply of external heat, that it is able to overcome the force of their mutual attractions, and, consequently, the molecules freely pass away from the surface of the liquid.

As will be seen from the illustrations given, namely, water and ether, the temperatures at which the vapours of different liquids exert a pressure equal to that of the atmosphere are widely different. This fact will be still more evident from the following table, giving the temperatures at which the vapour pressure of various liquids is equal to the standard atmospheric pressure :—

Liquid hydrogen	−253°
Liquid oxygen	−182.5°
Liquid nitrous oxide	− 89.8°
Liquid sulphur dioxide	− 10°
Ethyl chloride	+ 11°
Carbon disulphide	47°
Water	100°
Aniline	182°
Mercury	358°

Since the boiling-point of a liquid is that temperature at which its vapour-tension is equal to the atmospheric pressure, it will be evident that, if the latter increases or decreases, the temperature necessary to produce an equal vapour-pressure must also rise or fall; in other words, the boiling-point of a liquid is dependent upon the pressure. If a quantity of water, no warmer than the hand, be placed beneath the receiver of an air-pump, which is then quickly exhausted, the water will be seen to enter into violent ebullition. It does this when the pressure within the receiver is reduced to the point at which it is equal to the tension of aqueous vapour at the temperature taken.

For this reason water boils at a lower temperature in high altitudes than at the sea-level ; and as the vapour-tension of water at various temperatures has been experimentally determined, we can, by ascertaining the boiling-point of water at any particular altitude, calculate the atmospheric pressure, and consequently the height above the sea-level.

Many liquids when heated, especially in glass vessels that have been carefully cleansed, may be raised several degrees above the boiling-point without ebullition taking place. The liquid under these circumstances assumes a pulsating movement, which continues for a short time, when a burst of vapour is suddenly evolved with violence, and the temperature at once drops to the boiling-point. The liquid then becomes quiescent, and again as the temperature rises the pulsating movement begins, ending once more in an explosive evolution of vapour. This *successive* boiling, or *bumping*, is sometimes sufficiently violent to cause the fracture of the vessel. In order to experimentally ascertain the boiling-point of a liquid, the thermometer, for this reason, is not immersed in the *liquid*, but is suspended in the vapour, the temperature of which remains constant throughout these irregularities in the boiling.

Latent Heat of Vaporisation.—When a liquid is heated, its temperature rises, as indicated by the thermometer, until a certain point is reached (the boiling-point of the liquid), when the continued application of heat causes no further rise of temperature. Thermometers placed in the liquid, and in the vapour, indicate the same temperature and remain constant, and all further application of heat is unappreciated by these instruments, and disappears in changing the liquid into vapour. The heat which in this way is absorbed during the vaporisation of a liquid is spoken of as the *latent heat of vaporisation;* and the same amount of heat which thus disappears during the conversion of a liquid into a vapour is again rendered sensible when the vapour passes back into the liquid state.

The heat which is thus said to become *latent* is in reality converted into kinetic energy; it is expended in imparting to the molecules the kinetic energy necessary to overcome the attractive forces operating between them while in the liquid state; in other words, it is doing the work of overcoming cohesion (internal work), and also the external pressure on the vapour (external work).

FIG. 14.

In order that a liquid may pass into a vapour it is necessary that heat be absorbed. We have seen (page 126) that a liquid undergoing spontaneous evaporation becomes colder (that is, heat is absorbed by the molecules that are converted into the gaseous state), and also that the more rapidly the liquid can be made to pass into the vaporous condition, without supplying external heat, the lower will its temperature fall. Upon this fact depend a number of methods for the artificial production of low degrees of cold. For example, ether boils at 35°, but if a small quantity of ether be placed in a glass flask standing upon a wooden block, upon which a few drops of water have been poured, and a current of air from a bellows be briskly blown through the ether (Fig. 14), the temperature of the ether will fall so rapidly that in a few moments the flask will be frozen to the block. By the rapid evaporation of liquids with lower boiling-points, the extreme degrees of cold necessary for the liquefaction of such gases as oxygen, carbon monoxide, air, &c., are obtained. Thus, liquid methyl chloride boils at −23°; by causing it to rapidly vaporise, its temperature can be reduced to −70°. Liquid ethylene in the same way falls to a temperature of −120°, and liquid oxygen by rapid evaporation gives a temperature as low as −210°.

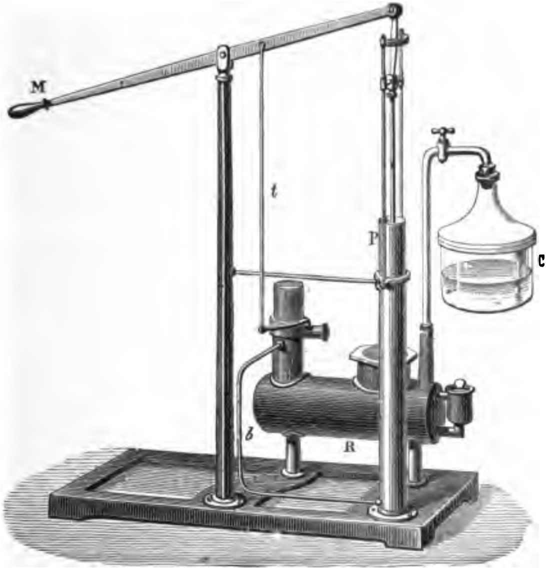

FIG. 15.

The temperature of water, in like manner, may be so lowered by its own rapid evaporation, as to cause it to freeze. We have already seen that by reducing the pressure, the boiling-point of a liquid is lowered; if, therefore, a quantity of water be placed in a vacuum, and methods be adopted to remove the water vapour as rapidly as it is formed, the water will enter into rapid ebullition. The evaporation will therefore proceed so rapidly, and consequently absorb heat so quickly, that the temperature of the boiling liquid will quickly fall to 0° when it passes into the solid state. The instrument known as Carré's freezing machine depends upon this principle. The water to be frozen is placed in the glass bottle C (Fig. 15), which is in connection with a metal reservoir R, half filled with strong sulphuric acid. This in its turn is connected by *b* with an air-pump P, worked by the lever M, to which is also attached a connecting rod *t*, so that a stirrer within the reservoir is kept constantly in motion. As soon as the apparatus is exhausted to a pressure of two or three millimetres, the water begins rapidly to boil, and as the sulphuric acid absorbs the water vapour as rapidly as it is given off, the temperature quickly falls and the water freezes.

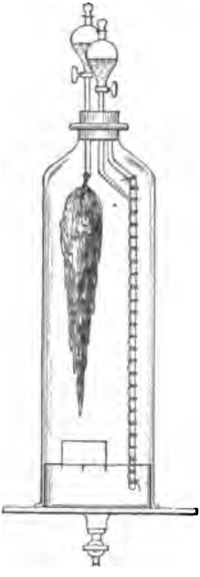

FIG. 16.

Fig. 16 illustrates another method by which the same result may be obtained. A tall glass vessel is exhausted by means of an ordinary air-pump, and water is allowed slowly to enter from a stoppered funnel, upon the end of which is secured a short string. At the same time strong sulphuric acid is admitted by the second funnel, and caused to flow down a glass rod, round which is wound a spiral of asbestos thread. The acid at once absorbs the aqueous vapour from the evaporating water, the temperature of which, therefore, falls below the freezing-point, and it solidifies as it flows over the string into the form of an icicle.

Just as diminution in pressure lowers the boiling-point of a liquid, so increased pressure raises the boiling-point. If water be heated in a closed iron vessel, as in a high-pressure steam boiler, the pressure caused by its own vapour raises the boiling-point many degrees above 100°. There is a definite temperature, however, for every liquid, beyond which the liquid state is impossible, whatever may be the pressure; that is to say, the liquid when heated beyond this fixed point passes into the gaseous state, however great the pressure may be. This temperature is the *critical temperature* (see page 79). If a liquid be heated in a sealed and strong glass tube, as the critical temperature is approached the surface of the liquid gradually becomes ill-defined, and finally the tube is completely occupied by transparent vapour. On again cooling, as soon as the critical point is passed the contents of the tube again separate into two distinct layers consisting of liquid and gas.

Vapour-Pressures of Solutions.—The boiling-point of a liquid is modified by the presence in the liquid of dissolved substances. If the substance in the solution be less volatile than the liquid, the boiling-point is raised. Thus, while the boiling-point of pure water (under the normal atmospheric pressure) is 100°, the temperature at which saturated aqueous solutions of salts boil, is considerably higher, thus :—

Water Saturated with	Containing Grammes of Salt in 100 Grammes of Water.	Boiling-point.
Sodium chloride . . .	41.2	108.4°
Potassium nitrate . . .	335.1	115.9°
Potassium carbonate . .	205.0	133.0°
Calcium chloride . . .	325.0	179.5°

The temperature of the steam of these boiling solutions, as ascertained by suspending a thermometer in the vapour, appears to be the same as that from pure water, as the thermometer in all cases indicates 100°. In reality, however, the temperature is higher, although not so high as that of the boiling liquid. The reason that the thermometer indicates 100° in all cases is because the water vapour continually condenses upon the bulb of the instrument, covering it with a film of pure water, which boiling off from the bulb indicates only the boiling-point of the pure liquid. By special arrangements this condensation may be prevented, when it has been shown (Magnus) that the temperature of the vapour, from such boiling solutions, rises as the solutions become more concentrated—that is, as the temperature of the boiling liquids rise. It has been already explained that the boiling-point of a liquid is that temperature at which the vapour tension is equal to the atmospheric pressure; since, then, the presence of dissolved substances raises the boiling-point, it follows that it must lower the vapour-pressure, for (in the case of aqueous solutions) when the temperature has reached 100° the vapour-pressure is still below that of the atmosphere, for the liquid does not enter into ebullition at that temperature. *Lowering* the vapour-pressure, therefore, is synonymous with *raising* the boiling-point. The extent to which the vapour-pressure of a liquid is lowered (or its boiling-point raised) by dissolving in 100 grammes of it 1 gramme-molecule of a given substance is called the *molecular lowering* of the vapour-pressure, or the *molecular elevation* of the boiling-point of that liquid. Now it has been found with substances which do not undergo ionic dissociation in the solvent employed, and also which do not themselves exert any appreciable vapour-pressure at the boiling-point of the solvent, that this molecular lowering of the vapour-pressure is practically a constant. Thus, for water the molecular rise of boiling-point is 5.2°; while for benzene it is 27.0°.

For example, given two substances, say glycerol and sugar, which, when dissolved in water, yield solutions which are non-electrolytes (*i.e.* these compounds do not dissociate), and are also themselves practically non-volatile at the boiling-point of water; then, if 1 gramme-molecule of each be separately dissolved in 100 grammes of water, the two solutions obtained will be found to boil at about 105.2° instead of 100°. Or again, two substances fulfilling the same conditions when dissolved in benzene would send up the boiling-point of this liquid from 80.5° to 107.5°.

If, on the other hand, the substance is an electrolyte—that is, one which undergoes ionic dissociation in the solvent, then the effect produced by the same weight of substance is greater, since the ions behave as though they were molecules, and the result is the same as though a larger number of molecules were present in the solution. Obviously the increase in the effect produced will depend upon the extent to which dissociation takes place.

The following general laws relating to the effect of dissolved substances upon vapour-pressure have been established:—

1. *The relation between the quantity of a substance in solution and the diminution of the vapour-pressure below that of the pure solvent is the same at all temperatures.*

2. *The diminution of the vapour-pressure of a liquid, by a dissolved substance, is proportional to the amount of the substance in solution (provided the substance itself exerts no appreciable vapour-pressure at the temperature of the experiment).*

3. *The molecular lowering of vapour-pressure by chemically similar substances is constant; that is to say, solutions containing one molecular weight in grammes (one gramme-molecule) of such substances in equal volumes of the solvent, give rise to the same diminution of vapour-pressure.*

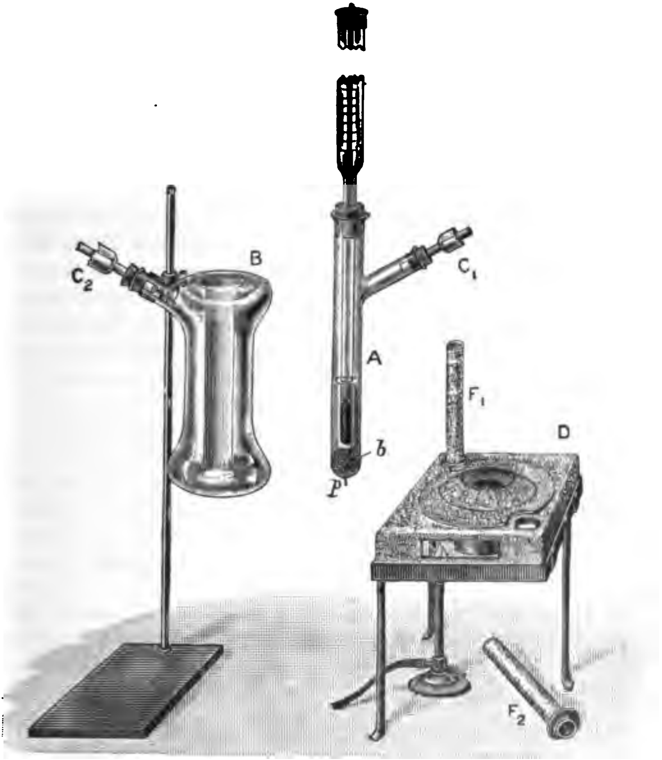

FIG. 17.

4. *The relative lowering of vapour-pressure is proportional to the ratio of the number of molecules of the dissolved substance, to the total number of molecules in the solution, i.e. the sum of the number of molecules of the dissolved substance and of the solvent.**

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* Except in the case of electrolytes. See page 109.

Upon these considerations it becomes possible, by means of the lowering of the vapour-pressure, to determine the molecular weight of a substance that is capable of being dissolved in a volatile liquid.

The apparatus in which such a determination is made is shown in dissected form in Fig. 17. A weighed quantity of the solvent to be employed is contained in the tube A which is inserted in the vessel B, which in its turn is placed upon the asbestos support D, and heated from below by means of small flames. As the liquid in A boils, its vapour is condensed by the condenser indicated at C_1, and thereby returned to the vessel. The outer vessel B also contains a small quantity of the same liquid which boils simultaneously, so that the inner tube is thus surrounded by a jacket filled with the hot vapour of the same liquid as is boiling inside. The vapour from the boiling liquid in this jacket vessel is condensed by the condenser at C_2 and constantly returned. By means of a thermometer the exact temperature at which the liquid boils is thus ascertained, after which a weighed quantity of the substance whose molecular weight is to be determined is introduced and the boiling-point again ascertained.

The result is calculated by the formula—

$$M = \frac{Cg.}{R}$$

When C = Constant—namely, the molecular elevation of the boiling-point of the solvent used ;

g = The percentage strength of the solution ; and

R = The observed rise of boiling-point.

The Passage of Liquids into Solids.—Most liquids, when cooled to some specific temperature, pass into the solid state ; the temperature at which this change takes place is termed the solidifying point. Generally speaking, the temperature at which a liquid solidifies is the same as that at which the solid again melts ; but as the solidification of a liquid is subject to disturbances from causes that do not affect the melting-point, this is not always the case. Thus, water may be cooled many degrees below 0° if it be previously freed from dissolved air, and be kept perfectly still. This super cooling of water may readily be illustrated by means of the apparatus represented in Fig. 18. This consists of a thermometer whose bulb is enclosed in a larger bulb containing water, which before the bulb is sealed at *a*, is briskly boiled to expel all the air.

When the instrument is immersed in a freezing mixture the temperature of the water may be lowered to −15° without congelation taking place, but on the slightest agitation it at once solidifies and the temperature rises to 0°. It is on account of this property of water to suspend its solidification, that in determining the lower fixed point of a thermometer, the temperature of melting ice, and not that of freezing water, is made use of.

Many other liquids exhibit suspended solidification to a very high degree; thus glycerine may be cooled to −30° or −40° without solidifying, but if a crystal of solid glycerine be placed in the liquid the entire mass freezes, and does not again melt until a temperature of 15.5° is reached.

Change of Volume on Solidification.—Most liquids, in the act of solidifying, contract; that is to say, the solid occupies a smaller volume than the liquid. Consequently the solid is specifically denser, and sinks in the liquid. Thus 100 volumes of liquid phosphorus at 44° (the melting-point) when solidified occupy only 96.7 volumes. Water expands upon solidification, hence ice is relatively lighter than water, and floats upon the liquid. The reverse change of volume accompanies the change of state in the opposite direction.

Effect of Pressure upon the Solidifying Point of Liquids.—In the case of liquids that contract upon solidification, increased pressure raises the point of solidification, and consequently raises the melting-point of the solid. The effect, however, is extremely small: thus the solidifying-point (and melting-point) of spermaceti under the standard atmospheric pressure is 47.7°, while under a pressure of 156 atmospheres it is raised to 50.9°.

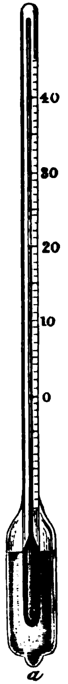

FIG. 18.

With liquids that expand on solidification, increased pressure has the opposite effect, and lowers the solidifying point. Thus, water under great pressure may be cooled below 0° and still remain liquid; and in the same way ice may be liquefied by increased pressure without altering its temperature. In the case of water it has been found that an increased pressure of n atmospheres lowers the solidifying point by $0.0074n°$; hence under a pressure of 135 atmospheres, the freezing-point of water (and the melting-point of ice) is lowered 1°. This lowering of the melting-point of ice under pressure may be illustrated by the experiment represented in Fig. 19. Over a block of ice is slung a fine steel wire, to which are hung a number of weights. The pressure thus exerted upon the ice, by lowering the melting-point, causes the ice to liquefy immediately beneath the wire, which therefore gradually cuts its way through the block. But as the wire passes through the mass, each layer of water behind it again resolidifies, being no longer subject to the increased pressure; hence, although the wire cuts its way completely through the ice, the block still remains intact.

Latent Heat of Fusion.—When a liquid, at a temperature above its solidifying point, is cooled, a thermometer placed in the liquid indicates its loss of heat until solidification begins. At this point the temperature remains constant until solidification is complete, when the thermometer again begins to fall. And again, when a solid, at a temperature below its melting-point, is heated, its temperature rises until the melting begins, but no further rise of temperature takes place by the application of heat until liquefaction is complete. The sensible heat that so disappears during fusion is spoken of as the *latent heat of fusion.* Just as in the passage of liquids into gases, this so-called latent heat represents heat that has ceased to be *heat*, but which is converted into kinetic energy that is taken up by the molecules: when the liquid passes back into the solid state, this energy is again transformed into sensible heat.

FIG. 19.

The fact that heat is thus changed into energy, and so rendered insensible to the thermometer, may be seen by adding boiling water to powdered ice. A thermometer placed in ice indicates the temperature 0°, and although boiling water is poured upon it, so long as any ice remains unmelted no rise of temperature of the mixture results, the heat contained in the boiling water being expended in doing the work of liquefying the ice, and converting it into water at 0°.

When such an experiment is made more exactly, it is found that 1 kilogramme of water at 80.25°, when mixed with 1 kilogramme of ice at 0°, gives 2 kilogrammes of water at 0°. That is to say, the amount of heat contained in a kilogramme of water at 80.25° is exactly capable of transforming an equal weight of ice at 0° into water at 0°.

As the heat required to raise the temperature of 1 kilogramme of water from 0° to 1° is the unit of heat, or *major calorie*, we say that the latent heat of fusion of ice is 80.25 thermal units or calories.

During the solidification of a liquid, the latent heat of fusion is again given out. The solidification, therefore, only takes place gradually, for the heat evolved by the congelation of one portion is taken up by the neighbouring particles, whose solidification is thereby retarded until this heat is dissipated. In the case of super-cooled liquids and super-saturated saline solutions, the solidification takes place more suddenly, and the evolution of the latent heat is therefore manifest by a rise of temperature.

Effect of Substances in Solution upon the Solidifying Point of a Liquid.—It has long been known that a lower degree of cold is necessary to freeze salt water than fresh ; and also that the water obtained by remelting ice from frozen sea-water is so little salt as to be drinkable. Quantitative experiments show that water containing 1 per cent. of common salt requires to be cooled to −0.6° before the water begins to freeze ; and, moreover, that when such a dilute solution begins to freeze, the solid which separates out is *not* the salt, but is *pure ice*. This also holds in the case of all other solvents that are capable of being solidified, the pure solidified solvent alone separating when the solution is frozen. For instance, benzene freezes at 6° ; but if a small quantity of any substance which it is capable of dissolving be added (either a solid or liquid substance), it will be found necessary to cool the liquid *below* 6° before the benzene begins to freeze. The effect of dissolved substances in lowering the solidifying point of the solvent was first discovered by Blagden (1788), who formulated the law that the depression of the freezing-point of aqueous solutions of the same substance was proportional to the strength of the solution. By referring the lowering of the solidifying point to quantities of the dissolved substances that were in molecular proportions, instead of to equal weights, it has been found that in the case of certain chemically allied substances the following general law holds good: *Solutions containing in equal volumes of the solvent quantities of* *dissolved substances proportional to their molecular weights have the same point of solidification.*

Thus, centi-normal solutions of sodium chloride and potassium chloride (*i.e.* solutions containing 0.585 gramme NaCl and 0.746 gramme KCl respectively in one litre of water) will begin to freeze at the same fraction of a degree below 0°. In other words, the depression of the freezing-point of the solvent is a function of the *number of molecules* of the dissolved substance, irrespective of the nature of the molecules. The extent to which the freezing-point of a liquid would be depressed* by dissolving in 100 grammes of it one gramme-molecule of any substance is called the *molecular depression* of the freezing-point of that liquid, and it is found that in the case of all substances which are non-electrolytes, *i.e.* which do not undergo ionisation, this molecular depression for a given liquid is practically a constant. Thus in the case of water, when the substance dissolved is a non-electrolyte, the molecular depression is about 18.5°.

In the case of substances which dissociate into their ions in the solution, the molecular depression will be greater, depending upon the degree of ionisation. Thus in the case of strong acids, bases, and salts, that is, "electrolytes" which undergo dissociation to the highest degree, it is found that the molecular depression is practically double that given by non-electrolytes. The ions in the liquid acting as independent molecules, it will be obvious that if dissociation is complete there will be twice as many ions as there were molecules of the compound, and therefore the effect produced in respect of lowering the freezing-point should be twice as great. The relations thus established between the molecular weight of a compound and its influence in lowering the freezing-point of a solvent form the basis of a method for the determination of molecular weights (Raoult's method).

The process is carried out in a tube quite similar to tube A, Fig. 17 (the side tube in this case being merely closed with a cork). A weighed quantity of the solvent is introduced into this tube, which is then carefully cooled in a freezing-mixture, the liquid being gently stirred by means of a wire passing through a hole in the top cork. The temperature at which freezing begins to take place is noted. The tube is then withdrawn from the freezing-

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* In actually determining depressions of freezing-point, solutions so strong as this cannot be used. The determination is made with dilute solutions, and the *molecular* depression obtained by calculation.

mixture and the solidified portion allowed to melt, when a weighed quantity of the substance whose molecular weight is to be determined is introduced, and the operation repeated. The molecular depression is calculated from the formula—

$$m=\frac{Cg}{l},$$

where C=constant—the molecular depression of the freezing-point;
g=grammes of substances in 100 grammes of the solvent;
and l=the observed depression of the freezing-point.

CHAPTER XIV

SOLUTION

A SOLUTION may be defined as a homogeneous mixture of either a gas, a liquid, or a solid with a liquid, this liquid being termed the *solvent.*[*]

Substances that are capable of forming such homogeneous mixtures with a solvent are said to be soluble in that liquid. The solution of matter in its three states will be treated separately.

1. Solution of Gases in Liquids.—When a gas is dissolved by a liquid, the liquid is said to *absorb* the gas, and although it is held that most liquids are capable of absorbing most gases to a greater or less degree, most of the investigations in this direction have been made with the two liquids, water and alcohol, by Bunsen.

The quantity of a gas which a liquid is capable of absorbing depends upon four factors—(1) the specific nature of the liquid; (2) the nature of the gas; (3) the temperature of the liquid; (4) the pressure.

(1.) The influence of the solvent may be seen by a comparison of the quantities of the same gas which equal volumes of water and of alcohol are capable of dissolving, thus—

100 volumes of water at 0° dissolve 179.6 volumes of carbon dioxide,
while 100 ,, alcohol ,, 432.9 ,, ,,

(2.) The various quantities of different gases which the same liquid will absorb are found to extend over a very wide range, thus—

100 volumes of water at 0° dissolve 4.114 volumes of oxygen,
while 100 ,, ,, ,, 114800.0 ,, ammonia.

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[*] Mixtures of gases are sometimes regarded as solutions, one gas being said to be dissolved in the other. Gases also are sometimes spoken of as dissolving liquids and solids, when liquid and solid substances directly vaporise into them.

(3.) The volume of any gas which a liquid can absorb diminishes with a rise of temperature.* This will be seen from the following table, where the volumes of different gases are given which 100 volumes of water will absorb at various temperatures.

Temperature.	Carbon Dioxide.	Nitrous Oxide.	Oxygen.	Nitrogen.
0	179.6	130.5	4.11	2.03
5	144.9	109.3	3.62	1.79
10	118.4	91.9	3.25	1.60
20	90.1	67.0	2.83	1.40

It was at one time believed that the solvent power of water for hydrogen was the same at all temperatures between 0° and 25°. Recent experiments have shown, however, that there is no exception to the general law in this case; thus it has been found that 100 volumes of water—

At 0°	dissolve	2.15	volumes	of	hydrogen.
At 5°	„	2.06	„		„
At 10°	„	1.98	„		„
At 20°	„	1.84	„		„

When a solution of a gas in water is heated, the gas being less soluble at the higher temperature is expelled, and in most cases the whole of the gas is driven off at the boiling temperature. This, however, is not invariably the case; for example, the solution of hydrochloric acid in water, when boiled, will distil, without further evolution of gas, when a solution of definite strength is reached (see Hydrochloric Acid).

(4.) The influence of pressure upon the volume of a given gas which a liquid can absorb was discovered by Henry (1803), and is known as Henry's law, namely, *The volume of the gas absorbed by a liquid is directly proportional to the pressure of the gas.* If the pressure be doubled, the same volume of liquid will dissolve twice the volume of the gas, the volume in each case being measured at 0° and 760 mm. But since, according to Boyle's law, the volume of a gas is inversely as the pressure, this law may be thus stated: *A given volume of a liquid will absorb the same volume of a gas at all pressures.*

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* Helium, between certain limits of temperature, is an exception.

Thus, if 100 volumes of water at 0° dissolve 2.03 volumes of nitrogen, under the standard atmospheric pressure (the volume of the gas being measured at 0° and 760 mm.), under twice this pressure, *i.e.* two atmospheres, the same volume will absorb twice the volume of nitrogen, viz., 4.06 volumes *measured at* 0° *and* 760 *mm.* But 4.06 volumes of gas measured at 0° and 760 mm. occupy 2.03 volumes under a pressure of two atmospheres, therefore the liquid dissolves the same volume of compressed gas as of gas under ordinary pressure.

Henry's law is sometimes stated in a slightly altered form. If the quantity of gas present in a unit volume of both the liquid and the space above it be called the *concentration* of the gas, then the law may be expressed by saying that *under all pressures, the ratio of the concentrations of the gas in the liquid, and in the space above it, remains constant.* This ratio is termed the *coefficient of solubility*, or the "solubility" of the gas in the particular liquid.

The term *coefficient of absorption*, first introduced by Bunsen, is the volume of the gas measured at 0° and 760 mm., which is absorbed by 1 cubic centimetre of a liquid at the same temperature and pressure; and it is therefore simply the volume representing the "solubility" of the gas, reduced to 0°.

The solubility of gases in liquids is measured by agitating a known volume of liquid with a measured volume of the gas, under determinate conditions of temperature and pressure. The apparatus employed by Bunsen, and known as Bunsen's absorptiometer, is shown in Fig. 20. It consists of a graduated tube *e*, into which known volumes of the gas and liquid are introduced. The lower end of this tube is furnished with an iron screw, by means of which it can be securely screwed down upon an indiarubber pad, in order to completely close the tube (seen in the side figure). The tube containing the gas and liquid under examination is lowered into a tall cylinder *g g*, in the bottom of which is a quantity of mercury. The cylinder is then filled with water, and the cap *p* screwed down. The thermometer *k* registers the temperature. The apparatus is then briskly shaken, in order that the liquid in the eudiometer may exert its full solvent action upon the gas, and on slightly unscrewing the tube from the caoutchouc pad, mercury enters to take the place of the dissolved gas. The tube is again closed and the shaking repeated, and these operations are continued until no further absorption results. Finally, the volume of gas is measured, the temperature noted, and the pressure

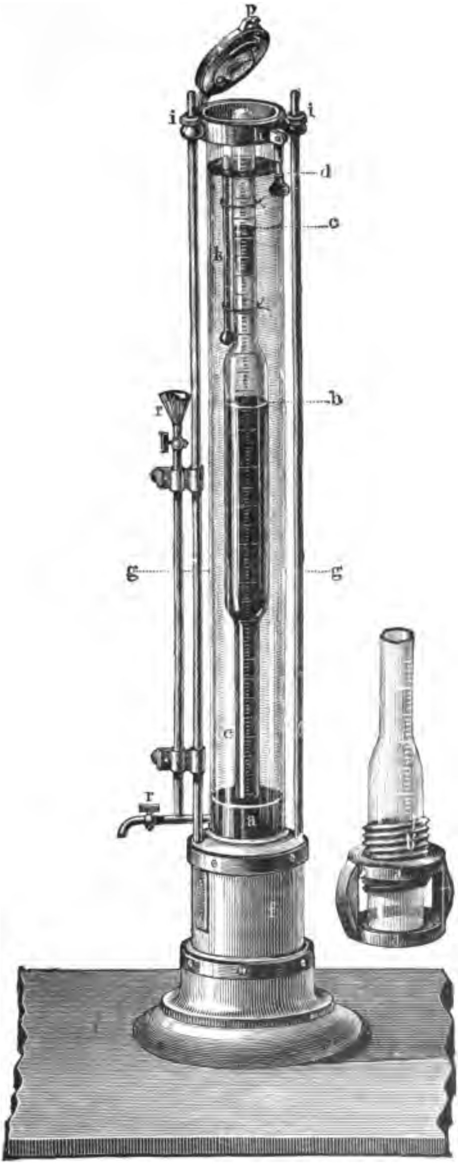

FIG. 20.

ascertained by reading the position of the mercury within the tube, and deducting the height of the column from *b* to the surface of the mercury a, from the barometric pressure at the time of making the experiment. The temperature of the water in the cylinder may be varied, and the coefficient of absorption at different temperatures can thus be determined.

Fig. 21 represents a more modern absorptiometer, being a modified form of Heidenhain and Meyer's apparatus. In this instrument the measuring tube and the absorption vessel are separate, and it admits of the use of much larger volumes of liquid. By means of the three-way cock *a*, the gas to be experimented upon is introduced into *A* by first raising and then lowering *B*; and the volume is measured when the levels of the mercury in *A* and *B* are coincident. By means of the three-way cock *b*, the vessel *C*, of known capacity, and which is connected with *A* by means of a flexible metal capillary tube, is filled with the desired liquid. The vessels *A* and *C* are then put into communication, and by raising *B* and opening the tap *c* a definite volume of the liquid is run out into a measuring vessel, which represents the volume of gas that enters. The gas and liquid are then thoroughly agitated, after which the gas is passed back into *A* by lowering *B*, and, when *A* and *C* are in communication, opening the tap *c* beneath mercury. By measuring the diminution in volume suffered by the gas, the volume absorbed by the known volume of liquid is obtained. The measuring tube and absorption vessel are kept constant at any desired temperature by surrounding them by water, or with vapours at known temperatures.

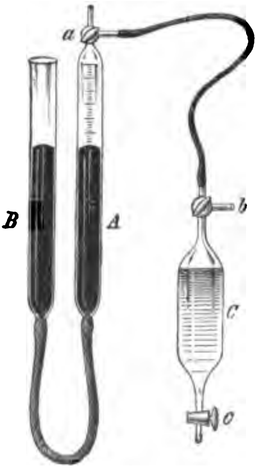

FIG. 21.

Solubility of Mixed Gases.—When two gases are mixed together, the pressure exerted by each is the same as would be exerted if the other were absent and the entire space were occupied by the same mass of the one. Thus, if a mixture of two gases are in the proportion of two volumes of one and one volume of the other, the pressure exerted by the one present in larger proportion will be twice as great as that of the other; this pressure is termed the *partial pressure* of the gas under the circumstances, and obviously the total pressure of the mixture will be the sum of the partial pressures of the constituents. As the solubility of a gas in a liquid is proportional to the pressure, the solubility of the gases in a gaseous mixture will be influenced by the proportions in which they are present in the mixture. This is known as Dalton's law of partial pressures, which may be thus stated: *The solubility of a gas in a gaseous mixture is proportional to its partial pressure.* For example, the atmosphere consists of a mixture of oxygen and nitrogen, in the proportion of four volumes of nitrogen to one volume of oxygen (in round numbers). The partial pressure exerted by the oxygen is therefore only one-fifth of the total atmospheric pressure, and consequently the amount of oxygen which a given volume of a liquid is capable of dissolving from the atmosphere is only about one-fifth of that which it will absorb from pure oxygen—in other words, will be one-fifth the absorption coefficient of oxygen for that liquid.

The application of the law of partial pressures will be seen in the solvent action of water upon the atmosphere. Taking the coefficients of absorption of oxygen and nitrogen for water as given by Bunsen—

$$\text{Oxygen} = .04114; \qquad \text{Nitrogen} = .02035,$$

and the proportion of oxygen to nitrogen in the air as one to four, by volume, we get—

$$\frac{.04114}{5} = .00823, \text{ and } \frac{.02035 \times 4}{5} = .01628,$$

for the number of cubic centimetres of oxygen and nitrogen which will be dissolved from the atmosphere by 1 cubic centimetre of water at 0°.

One hundred volumes of water, therefore, will dissolve 2.451 volumes of air, of which .823 volume is oxygen and 1.628 volumes is nitrogen; and if this dissolved air be again expelled from the water by boiling, the air so obtained will contain oxygen and nitrogen in the proportions—

Oxygen	33.6
Nitrogen	66.4
	100.0

If a mixture of oxygen and nitrogen in this proportion be once more dissolved in water, since the percentage of oxygen has risen from 20 to 33.6, and the partial pressure proportionately increased, the mixture of the two gases that will be dissolved will be still richer in oxygen ; and after solution in water for the third time the boiled-out air will be found to contain as much as 75 per cent. of oxygen. It will be obvious that the partial pressure which determines the extent to which the separate gases in a mixture are dissolved is not represented by the proportion in which the gases are present *before* solution, but that in which they exist in the gaseous mixture *after* the solvent has become saturated.

Henry's law does not hold good in the case of such very soluble gases as ammonia, hydrochloric acid, &c. These gases appear to enter into a true chemical union with the water, and in most of these cases the act of solution is attended with considerable evolution of heat. In some of these instances the deviation from the law diminishes with rise of temperature ; thus at temperatures above 40° the absorption of sulphur dioxide obeys the law, while in the case of ammonia conformity to the law is observed at 100°.

The gases dissolved by a liquid are not only expelled by boiling, but are withdrawn by placing the solution in a vacuum. This, indeed, follows from Henry's law, for if the solubility is proportional to the pressure, and the pressure is nil, the amount of gas dissolved must also be nil.

The molecules of gas dissolved by a liquid are regarded as being held by some attractive forces exerted between them and the molecules of the liquid ; in the course of their movements, gas molecules are constantly leaving and entering the liquid, and equilibrium is established when the same number enter and escape from the surface of the liquid in the same time. When the pressure is increased, more gas molecules strike the surface in a unit of time, and consequently a greater volume is absorbed. When a solution of a soluble gas is placed in an atmosphere of another gas, the dissolved gas continues to leave the liquid until equilibrium is established between the pressure exerted by the gas so leaving and the amount remaining in solution. For this reason a solution of ammonia, when left exposed to the air, rapidly becomes weaker, owing to the escape of the dissolved gas into the atmosphere. This process is accelerated if a stream of a less soluble gas be caused to bubble through the solution.

Solubility of Liquids in Liquids.—The solubility of liquids in liquids may be divided into two orders. First, cases in which the degree of solubility of one in the other is unlimited; and second, cases where the extent of the solubility is limited, or where the liquids are said to be *partially miscible*. Two liquids whose solubility in each other is unlimited are said to be *miscible in all proportions*; thus alcohol and water are capable of forming a homogeneous mixture when added together in any proportion.

In the second class, where the solubility of two liquids for each other is limited, it is found that each liquid is capable of dissolving some of the other. Thus, if equal volumes of ether and water are shaken together, the liquids will afterwards separate out into two distinct layers, one floating upon the other. The heavier layer at the bottom is an aqueous solution of ether, containing about 10 per cent. of ether; while the upper liquid is an ethereal solution of water containing about 3 per cent. of water. The presence of ether dissolved in the water may be proved by separating the two layers and gently heating the aqueous liquid in a small flask, when the dissolved ether will be expelled and can be inflamed. The presence of the water in the ether is also readily proved, either by introducing into the liquid a small quantity of dehydrated copper sulphate, which will rehydrate itself at the expense of the water in the ether, and be changed from white to blue; or by placing in the ethereal liquid a fragment of sodium, which decomposes the dissolved water with the liberation of hydrogen.

Another illustration of two partially miscible liquids is seen in the case of a strong aqueous solution of potassium carbonate and strong ammonia, which is of special interest as being the only example at present known of two aqueous solutions of inorganic substances which exhibit this phenomenon.* Thus, when strong aqueous ammonia (sp. gr. 0.880) is added to a concentrated solution of potassium carbonate, the two liquids separate from each other in two distinct layers, the upper layer consisting of ammonia which has taken up a certain amount of potassium carbonate, while the lower liquid consists of a solution of potassium carbonate which has dissolved a definite quantity of ammonia.

In most cases the solubility of liquids in liquids is increased by rise of temperature, although in some it is decreased. As an example of the former, the case of these two aqueous liquids may be quoted. If the temperature be raised then the solubility of each of these solutions in the other steadily increases, and the

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* Newth, *Trans. Chem. Soc.*, 1900, p. 775.

composition of the two layers will therefore gradually approximate until a point is reached at which they become identical. This point is arrived at when the temperature reaches about 43°, and at this temperature, therefore, the two liquids are *miscible in all proportions.* If this liquid be now cooled below this temperature, separation into the two *phases*, as it is termed, at once begins, and the liquid gradually becomes milky or turbid owing to the precipitation from it of the heavier solution in minute drops.

An instance of decreased solubility by rise of temperature is seen in the case of a mixture of triethylamine and water. If equal volumes of these liquids be mixed together, at a temperature below 20°, complete solution takes place, and a single homogeneous liquid results. On warming the solution it becomes turbid, owing to the separation of the liquid into two portions, which ultimately settle out as two distinct layers. As the temperature of the solution approaches 20°, the liquid becomes very sensitive to a slight rise of temperature, the heat of the hand being sufficient to cause turbidity in the solution.

It will be evident, therefore, from these considerations that the distinction between liquids which are *miscible in all proportions* and those which are only *partially miscible* is after all only an arbitrary one, the difference being simply a function of the temperature. It is, nevertheless, a convenient distinction to make, so long as we understand that it refers to liquids at the ordinary temperature.

Solution of Solids in Liquids.—When a solid is immersed in a liquid, the forces which oppose the solution of the solid are the attractive forces exerted by the molecules of the solid upon each other and those of the liquid upon themselves. The forces that tend to effect solution are the attractive forces exerted by the molecules of the liquid upon the molecules of the solid, and the kinetic energy of the molecules.

By the action of the liquid, the attractive force between the molecules of the solid is diminished, and those molecules nearest the surface, by their own energy and the attraction exerted by the liquid, pass into and through the liquid. In the course of their movements, these sometimes return to the solid, and a condition of equilibrium is finally established when as many molecules leave the surface of the solid as return to it in a given time. Under these circumstances the solution is said to be *saturated* with respect to the particular solid.

Saturated Solutions.—The amount of solid held in solution by the liquid when the latter is saturated depends upon the temperature, for if the temperature be raised, the kinetic energy of the molecules is increased, and consequently an increased number will become detached from the solid. As a general rule, therefore, the solubility of a solid in a liquid is increased by rise of temperature. A saturated solution at a given temperature may be obtained in two ways, namely, by maintaining the liquid at that temperature and stirring into it an excess of the solid, until no more of it is dissolved; or by dissolving a larger quantity of the solid at a higher temperature, and allowing the solution to stand in contact with an excess of undissolved solid, until the temperature falls to the specified point. During the cooling the amount of solid that the liquid had taken up, over and above that which was necessary to saturation at the lower temperature, is deposited.

Supersaturated Solutions.—The condition of saturation can only be determined when an excess of the undissolved solid is present in the liquid; for when a solution, which is not in contact with any of the undissolved solid, is brought to the point of saturation, either by cooling or by evaporation of the liquid, it frequently happens that no separation of solid takes place. Solutions can in this way be obtained, in which a larger amount of the solid remains dissolved at a given temperature than corresponds to the amount required to form a saturated solution at that temperature: such solutions are said to be *supersaturated.* If into such a supersaturated solution a fragment of the solid be introduced, molecules of the dissolved solid at once deposit themselves upon it, and this separation of the dissolved substance continues until the solution reaches a state of concentration corresponding to its normal saturation at the particular temperature. The introduction into a supersaturated solution of a particle of the solid, in respect to which the solution is supersaturated, is the only sure method of bringing about the separation of the excess of the dissolved substance; such a solution, therefore, may be preserved for an indefinite time, if it be kept in an hermetically sealed vessel. Minute particles of the solid towards which a solution is supersaturated, that might be present in the dust of the air, falling into such a solution, will determine the deposition of the dissolved solid.

The phenomenon of supersaturation is strictly analogous to that of supercooling, or the suspended solidification of fused solids, and is exhibited most readily by salts containing water of crystallisation, such as sodium acetate, $NaC_2H_3O_2,3H_2O$; sodium thiosulphate, $Na_2S_2O_3,5H_2O$; and sodium sulphate, $Na_2SO_4,10H_2O$. Thus, if a small quantity of water be poured into a flask nearly filled with crystallised sodium thiosulphate (the so-called "Hypo" of the photographer), and the mixture be warmed by immersion in hot water, the whole of the salt will dissolve; and if the solution be then allowed to cool undisturbed, it will assume the ordinary temperature, and still remain fluid. If into the supersaturated solution a crystal of the salt be dropped, the excess of salt present in solution

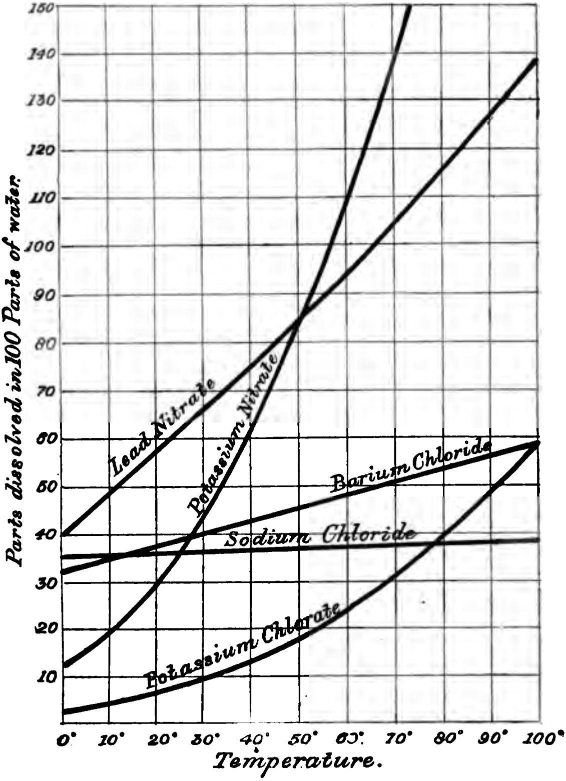

FIG. 22.

beyond the normal quantity for saturation at that temperature will crystallise out, and so great is this excess that the contents of the flask will appear practically solid.

The different solubility of various solids in the same liquid, and the increased solubility by rise of temperature, is graphically shown in Fig. 22, where the solubility curves of five salts in water are represented. The abscissæ indicate temperatures, and the ordinates the number of parts of salt dissolved by 100 parts of water.

Thus at 0° 180 grammes of water will dissolve 35.7 parts of sodium chloride, and as the temperature is raised the quantity of salt which the water will dissolve very slowly increases, until at 100° the amount is nearly 40 parts : sodium chloride is therefore nearly equally soluble in water at all temperatures.

In the case of potassium nitrate, 100 grammes of water at 0° will only dissolve 13.3 grammes of the solid, but as the temperature rises the amount capable of being dissolved by this quantity of water very rapidly increases, until at 75° 150 grammes are dissolved. Lead nitrate is more soluble than potassium nitrate between 0° and 50°, but above this point it is not so soluble as the other, hence the two curves intersect at that temperature. The solubility of sodium sulphate in water appears at first sight to be anomalous. The solubility at first rapidly increases with rise of temperature from 0°, and reaches a maximum at a point between 33° and 34°, when it gradually diminishes with further rise of temperature. This behaviour is in reality due to the fact that we are not dealing with one and the same substance throughout the experiment. Sodium sulphate exists as a solid in at least three forms, namely, the decahydrate, $Na_2SO_4,10H_2O$ (ordinary Glauber's salt) ; the heptahydrate, $Na_2SO_4,7H_2O$; and the anhydrous salt, Na_2SO_4. The first portion of the curve (Fig. 23) represents the solubility of Glauber's salt ; thus, at 20° such an amount of this decahydrated salt is dissolved, that the solution contains 20 grammes of Na_2SO_4 in 100 grammes of water. The solubility of this salt rapidly rises until 34° is reached, at which temperature the salt melts, and is then miscible with water in all proportions. The melted salt contains 78.8 parts of Na_2SO_4 in 100 parts of water, which is indicated as the highest point upon its curve :—

$$\overset{Na_2SO_4.}{\underbrace{23 + 23 + 32 + 64}_{142}} \qquad \overset{10H_2O.}{\underbrace{(2 + 16) \times 10}_{180}} \qquad 180 : 100 = 142 : 78.8.$$

The decahydrated salt is unable to exist as such at temperatures higher than 34°, and when the melted salt is heated above this point it is converted into the anhydrous salt and water saturated with the salt; therefore above 34° it is not possible to have a solution of sodium sulphate in contact with solid Glauber's salt. It can, however, be in contact with the anhydrous salt, and the second portion of the curve expresses the solubility of this compound in water, which slowly diminishes as the temperature rises.

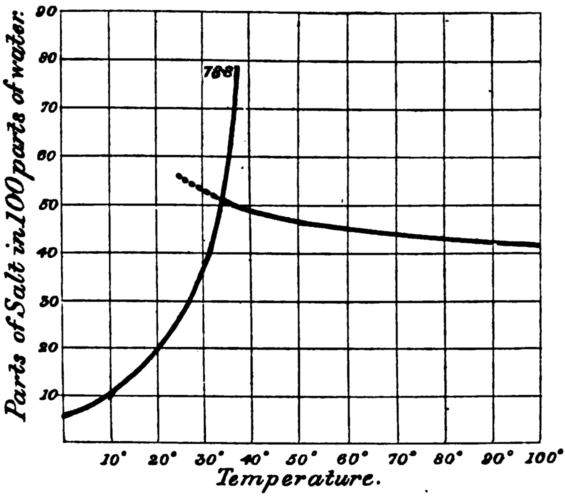

FIG. 23.

Paradoxical as it may at first appear, it is possible, by gradually cooling solutions of a salt in water, to cause them to become either more concentrated or more dilute according to circumstances. It has been already explained (page 139) that when a dilute solution of a salt in water is cooled below 0°, *ice only* separates out. Obviously, therefore, the solution that remains is more concentrated than at first, and its freezing-point will consequently be lowered. If the cooling be continued, more and more ice separates out, and the remaining liquid becomes gradually more and more concentrated until at length a point is reached when the solution is *saturated* for that particular temperature. If cooled below this point ice still separates, but as the solution would then be *super-*

saturated, salt also separates out; and the composition of the mixture of ice and salt which thus separates is the same as that of the remaining solution; in other words, the solution freezes as though it were a pure chemical compound of the water and the salt in solution.* Such a solution is known as a *constant-freezing* solution, or sometimes a *cryohydric* solution, and is comparable with such constant-boiling mixtures as are obtained by distilling either nitric or hydrochloric acids (see pages 239 and 367).

If now, instead of starting with a dilute solution, a concentrated solution is gradually cooled, at some particular temperature (depending upon the degree of concentration at first) the solution will become saturated for that temperature. Further cooling below this point will then cause the solution to deposit some of the salt; and the liquid, although still a saturated one as respects this lower temperature, will be more dilute. As the cooling continues, the separation of the salt continues, and the solution therefore becomes more and more dilute (still remaining saturated for the lower temperatures) until the point is reached when the solution is of such a strength that any further separation of salt (*i.e.* dilution) would yield a liquid which is below its own freezing-point. That is to say, the water itself now begins to freeze and separate along with the salt, and at this point the solution has reached the same constant-freezing condition as in the former case.

Osmotic Pressure.—When a dilute solution of a substance in water is placed in a vessel closed with an animal membrane, such as bladder (M, Fig. 24), and the whole is immersed in water to such a depth that the level of the water outside is coincident with that of the solution within, it is found that the liquid in the inner vessel increases in volume, as seen by the fact that it gradually rises in the narrow stem of the apparatus. Water, therefore, from the outer vessel must have passed in through the membrane, and inasmuch as some of the dissolved substance is found in the water of the outer vessel, some of the solution must at the same time have made its escape through the membrane. After the liquid has risen to a certain height in the narrow tube, it again begins to fall, as the contained solution continues to penetrate the membrane. This process is known as *endosmose*, and the instrument described is called an *endosmometer*.

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* At one time, indeed, such solutions were believed to contain definite chemical compounds of the salt with water, which were called *cryohydrates* (Guthrie).

Many attempts were made to establish general relations between the height to which the liquid rose in the narrow tube and the quantities of substance in the solution, but it was found impossible to obtain accurate or comparable measurements, for not only were the results disturbed by the effect of the constantly changing pressure upon the rate at which the dissolved substance escaped through the membrane, but different animal membranes yielded different results.

FIG. 24.

Semipermeable Membranes.—It was first discovered by Traube (1867), and afterwards extended by Pfeffer (1877), that artificial membranes, or pellicles, could be obtained, which, while allowing of the passage of water through them just as in the case of animal membranes, unlike these materials, they offered a perfect barrier to the passage of many substances in solution in the water. Such pellicles are known as semipermeable membranes. The material that has been found most suitable is precipitated copper ferrocyanide. If a solution of copper sulphate ($CuSO_4$) be brought cautiously in contact with a solution of potassium ferrocyanide ($K_4Fe(CN)_6$), at the point where the two liquids meet, a film or pellicle of precipitated copper ferrocyanide ($Cu_2Fe(CN)_6$) is produced. In order to make use of this extremely fragile membrane, Pfeffer devised the plan of precipitating it within the walls of a vessel made of unglazed porcelain. A small clay cylindrical cell, after thorough cleansing, was filled with a dilute solution of potassium ferrocyanide, and immersed in dilute copper sulphate. As these solutions entered the pores of the clay, and there met, a membrane, consisting of copper ferrocyanide, was formed within the walls, which under these circumstances was sufficiently strong to withstand a pressure of five or six atmospheres.

If such a cell, furnished with a semipermeable membrane, be employed as an endosmometer, and a dilute solution, say of sugar, be placed within the apparatus, which is then immersed in water, it is found that the liquid rises in the narrow tube to a certain height above the level of the water in the outside vessel, and remains stationary. Water passes through the membrane, but no dissolved substance passes out. At first more water penetrates inwards than passes out, hence the increased volume of liquid in the cell; but when a certain pressure is reached, represented by the height to which the liquid rises in the narrow tube, equilibrium is established, and water then passes in each direction at equal rates. The pressure at which this equilibrium is established is called the *osmotic pressure* of the solution.

Fig. 25 shows the apparatus employed by Pfeffer. *z* is the porous cell, in the walls of which the semipermeable membrane is precipitated. Into this are cemented the glass tubes *v* and *t*, the latter being attached, in the manner indicated, to a mercury manometer, *m*. When the cell containing a solution is immersed in water, the increased volume of the contained liquid that results causes a compression of the air enclosed in the upper part of the apparatus, which consequently drives up the mercury in the little manometer, which thus affords a means of measuring the osmotic pressure of the solution under examination.

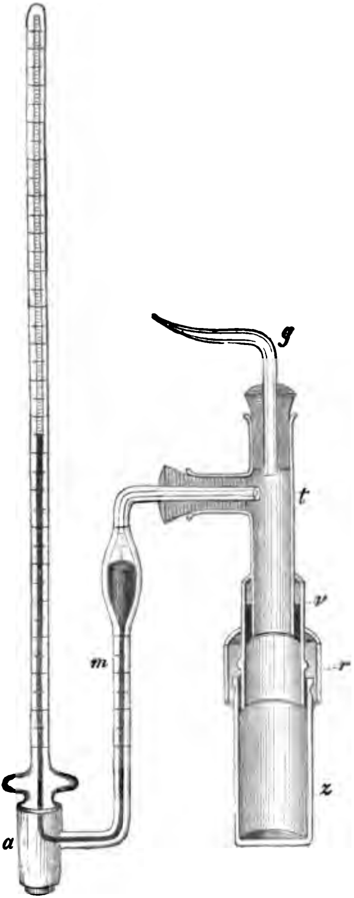

FIG. 25.

The following laws in relation to osmotic pressure have been established:—

1. Temperature and concentration being the same, different substances when in solution exert different pressures.

2. For one and the same substance, at constant temperature, the pressure exerted is proportional to the concentration.

3. The pressure for a solution of a given concentration is proportional to the absolute temperature,* the volume being kept constant.

4. Equimolecular quantities of different substances (*i.e.* quantities in the ratio of their gramme-molecule weights), when dissolved in the same volume of solvent, exert equal pressures at the same temperature.†

The analogy between these laws and those relating to gaseous pressure is very close. Thus the second statement corresponds with Boyle's law, when we consider the term *concentration* to denote the quantity of gas, that is, the number of molecules, in a given space; for if the number of molecules in a unit space be doubled, the gaseous pressure is doubled, and if the number of molecules of dissolved substance in a given volume of water be doubled, the osmotic pressure is doubled.

The third statement corresponds with the law of Charles: the volume of a gas is proportional to the absolute temperature; or, if the volume be maintained constant, the pressure exerted by a gas is proportional to the absolute temperature.

Osmotic pressure, therefore, just as gaseous pressure, increases with rise of temperature and diminishes with fall of temperature.

Again, in the last of these laws, we see the extension of Avogadro's hypothesis into the region of solution. Avogadro's hypothesis states that equal volumes of all gases contain (under similar conditions) an equal number of molecules—that is to say, an equal number of molecules at equal temperatures exert the same pressure. But an equal number of molecules of different gases represents an amount of the gases in the ratio of their molecular weights, hence Avogadro's hypothesis may be stated: equimolecular quantities of gases at the same temperature exert equal pressures; and this statement, as we have seen, is only true of molecules which do not dissociate when they pass into the gaseous state.

This close analogy between the gaseous laws and those regulating the behaviour of substances in dilute solution is explained on

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* By absolute temperature is meant the number of degrees above -273°·C.

† This is only true of those substances whose molecules neither dissociate into simpler forms (*i.e.* non-electrolytes), nor associate into more complex groups when in solution.

the assumption that the molecules of the dissolved body in a dilute solution are so far apart that their mutual attractive forces are reduced to a minimum, just as they are in the case of gaseous molecules, and that only such properties are exhibited by them as depend upon their number in a unit space. Further, it has been shown in the case of a dilute solution of sugar that the osmotic pressure (experimentally determined) is the same as the gaseous pressure that would be exerted by the weight of sugar present in the solution, if it were converted into gas and made to occupy the same volume as that occupied by the solution at the same temperature ; hence the general statement that *the pressure exerted by a substance in dilute solution* (*its osmotic pressure*) *is the same as would be exerted by the same amount of the substance if it existed as gas and occupied the same volume at the same temperature.*

Diffusion of Dissolved Substances.—If a quantity of a soluble solid substance be placed at the bottom of a vessel, which is then filled with water, the solid dissolves, and a layer of a strong solution is formed at the bottom. In time, however, the dissolved substance gradually diffuses throughout the liquid. This process of diffusion may be illustrated by means of the experiment represented in Fig. 26. At the bottom of the tall cylinder is placed a layer of a strong solution of ferric chloride, and upon this is carefully poured a quantity of water until the cylinder is nearly full. Upon the top of the water is then floated a solution of potassium thiocyanate in alcohol, and the whole is allowed to remain undisturbed. The ferric chloride will gradually diffuse up into the water, and the dissolved thiocyanate will diffuse down, and at the point where these salts meet they will interact chemically upon each, giving rise to a blood-red coloured solution, which will appear as a ring about midway down the cylinder.

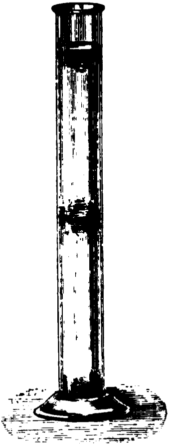

FIG. 26.

This phenomenon of the diffusion of dissolved substances is strictly comparable with the diffusion of gases, although in the former case the operation proceeds with extreme slowness. The force which impels the molecules of dissolved substances to diffuse is the osmotic pressure of the substance in solution.

The extension of the gaseous laws into the domain of solutions necessitates the hypothesis that in the case of some solutions the molecules of the dissolved substance unite to form more complicated molecular associations; while in other cases (including those substances which are electrolytes, such as the solutions of strong acids, bases, and salts) the molecules of the substances undergo dissociation into their *ions*. For, just as in the case of gases where departures from the strict gaseous laws are seen to take place, on account of the *dissociation* in some instances, and the *association* in others, of the various molecules, so it is believed that the deviations from the strict continuity of the ideal gaseous laws into the realm of solution are due to the operation of similar causes.

CRYSTALLINE FORMS.

When a saturated solution of a solid in a liquid is either cooled or allowed to evaporate, the dissolved solid begins to deposit itself out of the liquid, and it does so in most cases in definite geometric shapes, termed crystals. (Solids which exhibit no crystalline structure are said to be *amorphous*.)

The same arrangement of molecules into geometric forms often takes place also when substances in a state of *fusion* (as distinguished from *solution*) pass into the solid condition, as, for example, when melted sulphur, or mercury, or water are cooled to their respective solidifying points; and it also frequently takes place when vapours are condensed to the solid state. Speaking generally, the more slowly the process of solidification takes place, the larger and more geometrically perfect will be the crystals that are formed.

All the varieties of crystalline forms, both naturally occurring and artificially produced, are susceptible of classification into thirty-two classes,* based upon their symmetrical development with respect to certain imaginary planes, lines, and points, called respectively *planes of symmetry*, *lines of symmetry*, and *centres of symmetry*.

Planes of symmetry are planes cut through the crystal in such a direction that the two divided portions are the mirrored reflections the one of the other, the mirror being the plane itself. Crystals may have from 0 to 9 planes of symmetry; a cube, for example, has nine such planes.

Axes of symmetry are imaginary straight lines passing through the crystal in such a manner that when the crystal is rotated upon one of them there will be a complete recurrence of similar faces

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* The study of this classification belongs to the science of crystallography, and falls outside the scope of a general chemical text-book; it is therefore here treated only in broadest outline.

and angles at least *once* before an entire revolution has been made. For instance, if a tube is rotated upon an axes passing through the centre of one face at right angles to the face, it will obviously present the same appearance four times during a complete revolution. In thus being rotated through 360° crystals may exhibit this periodic reappearance of the same aspect, either two, three, four, or six times, and the axes are spoken of as *binary*, *trigonal*, *tetragonal*, and *hexagonal* respectively.* Crystals may possess from 0 to 13 axes of symmetry; the cube, for example, has thirteen such axes, *viz.* six binary, four trigonal, and three tetragonal.

Centres of symmetry. A crystal has a centre of symmetry when opposite to every face there is a precisely similar face parallel to it on the other side of the crystal.

Based upon these three orders of symmetry there are mathematically possible thirty-two classes into which crystals can be ranged; and with two or three exceptions only, crystals are known belonging to each class.

Crystallographic Systems. These thirty-two classes are susceptible of a further classification into the following six systems, based upon the relations of their crystallographic axes: †—

I. *Cubic* (*Regular* or *Isometric*) *System.* Crystals of this system are referred to three axes at right angles to each other, and all equal in length. The system includes five classes. Of these, that one which exhibits the highest degree of symmetry (spoken of as the *holohedral* or *normal* class) has nine planes of symmetry, thirteen axes of symmetry, and a centre of symmetry.

II. *Hexagonal System.* Forms of this system are referred to four axes: three are equal in length and intersect at angles of 120°, while the fourth, known as the *principal axis*, is different in length and is vertical to the others. Twelve classes are included in this system.‡ The normal or holohedral class has seven planes of symmetry, seven axes of symmetry, and a centre of symmetry.

III. *Tetragonal System.* Crystals belonging to this system are referable to three axes at right angles to each other, two being equal in length. The system includes seven classes, the holohedral class having five planes, five axes, and a centre of symmetry.

IV. *Orthorhombic* (*Rhombic* or *Prismatic*) *System.* Crystals are referred to three axes at right angles to each other, and all unequal in length. Three classes are included in this system, the holohedral class having three planes, three axes, and a centre of symmetry.

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* Sometimes the terms *diad*, *triad*, &c., are employed.

† Crystallographic axes do not necessarily correspond with axes of symmetry, although they are made to do so whenever possible.

‡ Seven of these classes consist of rhombohedral forms of this system, in which the *principal axis* is a trigonal axis of symmetry instead of being one of hexagonal symmetry. They are thus regarded as *hemihedral* (half the number of faces) modifications of the hexagonal form. Some crystallographers classify them as a separate system under the name of the *Rhombohedral* system.

V. *Monosymmetric* (or *Monoclinic*) *System.* In this system the forms are referable to three axes of unequal lengths, two of which intersect at an acute angle, while the third is at right angles to the other two. Two classes belong to this system, the holohedral class having one plane, one axis, and a centre of symmetry.

VI. *Asymmetric* (or *Triclinic*) *System.* Crystals are referred to three axes of unequal lengths, intersecting one another at oblique angles. Two classes are included in the system, the holohedral class having no planes or axes of symmetry, but a centre of symmetry only, while the second class has no element of symmetry at all.

One of the simplest forms in each of these six systems is the *double pyramid* (see Fig. 147 A). Thus there is the *tetragonal pyramid*, the *hexagonal pyramid*, and so on. In the case of the isometric or cubic system this double pyramid is called the *Octahedron.**

Another frequently recurring form common to all the systems except the cubic, is that of the *prism*, giving rise to *tetragonal prisms*, *hexagonal prisms*, &c.† Fig. 148 represents a group of natural crystals in the form of hexagonal prisms terminating in hexagonal prisms. Crystals, whether naturally occurring or artificially obtained, very seldom exhibit the perfect geometric shape of the ideal form, but usually exhibit more or less *distortion.* Fig. 110 (the left crystal) illustrates distortion in an orthorhombic pyramid. Fig. 147 A represents an octahedron which has developed into the perfect ideal form, but it is only by the greatest care in regulating their growth that such perfect crystals are obtained. In Fig. 147 B is seen the development of what is known as *twin crystals.* It very often happens that what would be an edge or a solid angle in the ideal crystal is replaced by a plane or planes. Such variations are called *truncations.* Illustrations of truncated crystals are seen in Fig. 110. In the right-hand crystal both apexes are truncated by planes or bases ; while in the other crystal one apex is truncated by a pyramid.

Two or more substances which crystallise in the same form are said to be *isomorphous ;* and on the other hand a substance which is capable of crystallising in two forms which do not belong to the same system is termed a *dimorphous* substance. Thus sulphur is dimorphous because it is capable of crystallising in *orthorhombic* pyramids and in *monosymmetric* prisms. Occasionally a dimorphous substance is isomorphous with another dimorphous substance in both its forms ; to this double isomorphism the term *isodimorphism* is applied.

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* The double pyramids of some of the other systems are also octahedra, in the sense that they possess eight faces, but in modern nomenclature the term *Octahedron* is reserved exclusively for the isometric pyramid.

† It will be obvious that a description of a crystal merely as being *prismatic* is incomplete without reference to the system to which it belongs.

CHAPTER XV

THERMO-CHEMISTRY

We have seen that by means of symbols and formulæ chemists express, in the form of equations, a certain amount of information respecting chemical changes: thus by the equation $C+O_2=CO_2$ there are conveyed the facts, that carbon unites with oxygen to form carbon dioxide, that 12 grammes of carbon combine with 32 grammes of oxygen, yielding 44 grammes of carbon dioxide, and that the volume of the gaseous carbon dioxide obtained is the same as that of the oxygen taking part in its formation. All such equations bear upon the face of them the truth, that matter can neither be destroyed nor created. The total *quantity* of matter taking part in the action is unaltered by the process, although it appears in altered form in the products of the reaction.

In all chemical changes, besides matter, *energy* also takes a part; not only do the materials concerned undergo rearrangement or readjustment, but at the same time there is a rearrangement or readjustment of energy. This energy change is not expressed by the ordinary symbolic equation. Thus in the equation—

$$SO_3+H_2O=H_2SO_4$$

the fact is embodied that 80 grammes of sulphur trioxide combine with 18 grammes of water and form 98 grammes of sulphuric acid; but the equation takes no cognisance of the fact, that when these weights of these two substances unite to form 98 grammes of sulphuric acid an amount of energy, in the form of heat, is disengaged that would raise the temperature of 213 grammes of water from 0° to the boiling-point.

Similarly, in the equation $2NCl_3=N_2+3Cl_2$ there is no recognition of the fact that during this change an enormous amount of energy leaves the system in the form of external work (overcoming the atmospheric pressure); in other words, that the conversion of nitrogen trichloride into its constituent elements is attended with the most violent explosion.

Energy, like matter, can neither be created nor destroyed, but as a result of chemical action it reappears as energy in another form. Thus it may appear as heat, as electrical energy, as kinetic energy, or as chemical energy; and just as the total amount of *matter* taking part in a chemical change reappears in altered form in the products of the change, so the disappearance of *energy* in any of its forms gives rise to the reappearance of a proportionate amount of energy in another form. This is the law of *the conservation of energy*, which may be thus stated:* "*The total energy of any material system is a quantity which can neither be increased nor diminished by any action between the parts of the system, although it may be transformed into any of the forms of which energy is susceptible.*"

Chemical energy, or that form of energy that is set free during chemical processes, cannot be measured by any direct method. This energy, however, is generally transformed, during chemical change, into heat, and may therefore be measured by, and expressed in, heat units. Thermo-chemistry may therefore be defined as the *science of the thermal changes which accompany chemical changes.*

All matter is regarded as containing a certain amount of energy in some form, and the purpose of thermo-chemistry is, by measuring the thermal disturbance that is conditioned by a chemical change, to ascertain the difference between the amount of energy contained in a system before and after such a change.

If all the energy of a system in its original state (*i.e.* before the chemical change takes place) that undergoes transformation into other forms of energy passes into heat; if none of it leaves the system as energy in some other form, and thereby escapes measurement; then the difference between the amount of energy contained in the system in its original and its final state may be ascertained. It by no means follows, however, that this represents the chemical energy alone; it has already been explained that chemical changes are always attended by physical changes, such as change of volume, of physical state, and so on, and we have also learned that such physical changes are likewise accompanied by thermal changes; the problem, therefore, is often a complicated one, and it is not always possible to differentiate between the chemical and the physical causes that may be operating simultaneously, and to decide what share of the final result is due to the chemical phase

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* Clerk Maxwell, "Matter and Motion."

of the change, and what to the physical change that simultaneously takes place.

As an illustration of the complex nature of chemical reactions when considered from a thermal standpoint, and of the disturbing effect of the accompanying physical changes, we may take the case of the action of aqueous hydrochloric acid upon crystallised sodium sulphate, $Na_2SO_4,10H_2O$—

$$Na_2SO_4,10H_2O+2HCl=2NaCl+H_2SO_4+10H_2O.$$

The chemical action here consists of (1) the decomposition of sodium sulphate, (2) the decomposition of hydrochloric acid, (3) the formation of sodium chloride, (4) the formation of sulphuric acid. Heat is absorbed by the first two portions of the action, and heat is evolved by the other two. The physical changes include the passage of ten molecules of water of crystallisation (*i.e. solid* water) into liquid water, and the solution of sodium chloride in water. These changes are attended with absorption of heat, and the net result of the entire change is the disappearance of a considerable amount of heat, that is to say, the thermal value of the reaction is a negative quantity.

The methods adopted in order to express thermo-chemical reactions are quite simple. The ordinary chemical symbols and formulæ are used, and represent, in all cases, quantities in grammes corresponding to the formula-weights of the substances. Thus Cl represents 35.5 grammes of chlorine; H_2O stands for 18 grammes of water, and so on. The chemical equation is followed by a number representing the quantity of heat, expressed in heat units, which is either produced or which disappears as a result of the change. The unit of heat is the *calorie*, or the quantity of heat that is capable of raising the temperature of 1 gramme of water from 0° to 1°. Sometimes the unit employed is the quantity of heat required to raise 1 gramme of water from 0° to 100°, and this unit (which is 100 times greater than the calorie) is indicated usually by the letter K. When heat is produced by a chemical change, the sign + is placed in front of the number of units, and when heat disappears, the fact is indicated by the sign −.

Thus the equation—

$$H_2+Cl_2=2HCl+44{,}000 \text{ cal.}$$

$$\text{or} \quad H_2+Cl_2=2HCl+440 \text{ K},$$

means that when 2 grammes of hydrogen combine with 71 grammes of chlorine to form gaseous hydrochloric acid, heat is disengaged to the amount of 44,000 calories, or 440 of the larger units, K. Or, in other words, that when these quantities of these substances combine, an amount of energy is lost to the system, represented by 44,000 calories. Therefore the energy possessed by 2 grammes of hydrogen and 71 grammes of chlorine is greater than that possessed by 73 grammes of hydrochloric acid gas by an amount which is represented by 44,000 gramme-units of heat. Hence the equation may be written—

$$\mathrm{2HCl} = \mathrm{H_2} + \mathrm{Cl_2} - 44{,}000 \text{ cal.}$$

which signifies that when 73 grammes of gaseous hydrochloric acid are decomposed into chlorine and hydrogen, it is necessary to supply an amount of energy equal to 44,000 calories.

In order to indicate the state of aggregation of the different substances, the method introduced by Ostwald consists in the use of different type, thick type being employed to denote solids, ordinary type indicating liquids, and italics signifying gases, thus—

$$\mathbf{C} + O_2 = CO_2 + 97{,}000 \text{ cal.}$$

means that the total energies of 12 grammes of solid carbon and 32 grammes of gaseous oxygen is greater than the energy possessed by 44 grammes of gaseous carbon dioxide by an amount equivalent to 97,000 calories.

Or, again, the equation—

$$\mathbf{SO_3} + \mathrm{H_2O} = \mathrm{H_2SO_4} + 21{,}320 \text{ cal.}$$

signifies that 80 grammes of solid sulphur trioxide unites with 18 grammes of liquid water and forms 98 grammes of liquid sulphuric acid, with the liberation of 21,300 gramme-units of heat.

Similarly, the heat evolved by the passage of water into ice, and the heat that disappears when water passes into steam, may be expressed by the equations—

$$\mathrm{H_2O} = \mathbf{H_2O} + 1440 \text{ cal.}$$
$$\mathrm{H_2O} = H_2O - 9670 \text{ cal.}$$

when water takes a direct part in the chemical change, as, for example, in the action of sulphur trioxide and water already quoted, the formula represents a gramme-molecule just as in all other cases ; but where the presence of a large quantity of water affects the thermal result of the chemical change, by exerting, for example, a solvent action, the symbol Aq is employed to signify that the presence of the water is considered in the thermal expression.

Thus the expression—

$$HBr + \mathrm{Aq} = \mathrm{HBrAq} + 19{,}900 \text{ cal.}$$

signifies that when 81 grammes of gaseous hydrobromic acid are dissolved in a large excess of water, 19,900 calories are evolved.

Again, the equation—

$$H_2 + Br_2 + \mathrm{Aq} = 2\mathrm{HBrAq} + 64{,}000 \text{ cal.}$$

means that when 160 grammes of gaseous bromine combine with 2 grammes of hydrogen, and the product is dissolved in an excess of water (*i.e.* such a quantity of water that no thermal change is produced by the addition of any further quantity), 64,000 calories are disengaged. Of this 64,000 calories, $19{,}900 \times 2 = 39{,}800$ are due to the solution of the twice 81 grammes of hydrobromic acid, and the difference, viz., 24,000 calories, represent the heat produced by the combination of 2 grammes of hydrogen with 160 grammes of bromine.

If water is formed as one of the products of the chemical reaction taking place in the case of substances in aqueous solution, such as when a solution of hydrochloric acid is added to a solution of sodium hydroxide, $\mathrm{HCl} + \mathrm{NaHO} = \mathrm{NaCl} + \mathrm{H_2O}$, as the water so produced simply mixes with the water in which the materials are dissolved, without producing any thermal effects by so doing, it is usually neglected in energy equations ; although, as already stated (page 109), when explained from the standpoint of the ionic theory, the heat of neutralisation is here due to the formation of molecules of water by the union of $\mathrm{H}^{\cdot}$ ions with HO' ions. Thus the above action may be expressed—

$$\mathrm{HClAq} + \mathrm{NaHOAq} = \mathrm{NaClAq} + 13{,}736 \text{ cal.}$$

The heat that is produced, or that disappears, in a chemical change which results in the formation of a particular compound is termed the *heat of formation* of that compound. Thus in the equation—

$$H_2 + Cl_2 = 2HCl + 44{,}000 \text{ cal.}$$

the heat of formation of 73 grammes of hydrochloric acid is 44,000 thermal units. This number, however, is in reality the algebraic sum of three quantities. It does not express merely the heat developed by the simple union of chlorine and hydrogen. The chemical change expressed by the equation consists in reality of three operations—

$$(1.)\ H_2 = H + H. \quad (2.)\ Cl_2 = Cl + Cl. \quad (3.)\ Cl + Cl + H + H = 2HCl.$$

Each of these operations represents a distinct thermal effect; in Nos. (1) and (2) heat is absorbed, in No. (3) heat is evolved, and calling these values h_1, h_2, and h_3, we have as the net result $h_3 - (h_1 + h_2) = 44{,}000$ cal.

The number of heat-units, therefore, which expresses the heat of formation of hydrochloric acid is the heat produced by the union of two atoms of hydrogen with two atoms of chlorine, minus the heat absorbed in the decomposition of one hydrogen and one chlorine molecule.

Compounds such as hydrochloric acid, in the formation of which heat is developed, are termed *exothermic* compounds, the reaction by which they are produced being an exothermic change; compounds, on the other hand, whose heats of formation are expressed by a negative sign, that is, in whose formation heat disappears, are distinguished as *endothermic compounds*, and the reactions by which they are formed are endothermic reactions.

Thus $$C + S_2 = CS_2 - 19{,}600 \text{ cal.},$$

signifies that in the formation of carbon disulphide heat is absorbed, and the compound is therefore an endothermic compound.

Thermo-chemical determinations are made by means of instruments termed calorimeters. These are of great variety, although the principle involved is the same. The chemical reaction is caused to take place under such circumstances, that the whole of the heat that is liberated shall be communicated to a known volume of water, at a known temperature.*

Direct determinations of the thermal value of chemical changes have hitherto been made in only a limited number of comparatively simple cases; it is possible, however, from a few known data, to calculate the thermal values of a number of changes which cannot be directly measured. This depends upon the fundamental principle

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* For descriptions of the various calorimeters, see treatises on Physics.

of thermo-chemistry, which is itself the corollary of the law of the conservation of energy, and which was first experimentally proved by Hess (1840). This principle, which is sometimes termed the *law of constant heat consummation*, or the *law of equivalence of heat and chemical change*, may be thus stated: The amount of heat that is liberated or absorbed, during a chemical process, is dependent solely upon the initial and final states of the system, and is independent of the intermediate stages. The following examples will serve to explain the application of the principle:—

1. Let us suppose it is desired to find the heat of formation of carbon monoxide, the data at our disposal being (1) the heat produced when carbon unites with oxygen to form carbon dioxide; and (2) the heat formed by the combustion of carbon monoxide to carbon dioxide. The thermal equations are—

$$(1)\ C+O_2=CO_2+97{,}000 \text{ cal.}$$

$$(2)\ 2CO+O_2=2CO_2+136{,}000 \text{ cal.}$$

Halving the second equation, in order to get the heat produced in the formation of 44 grammes of carbon dioxide (*i.e.* the same weight as in the first), we may represent the equation as—

$$CO+O=CO_2+68{,}000 \text{ cal.}^*$$

The difference between the two values 97,000 and 68,000 will be the heat of formation of carbon monoxide, therefore we get the equation—

$$C+O=CO+29{,}000 \text{ cal.}$$

2. The compound, methane (marsh gas), CH_4, cannot be formed by the direct union of its elements, but its heat of formation can be calculated by the application of this principle. The data in this case are the ascertained heats of formation of carbon dioxide

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* It must be remembered that this equation does not express the whole truth: as it here stands it would imply that 68,000 calories represent the heat formed by the simple chemical union of 28 grammes of carbon monoxide with 16 grammes of oxygen. In reality this number is half the sum of the two values, namely, the heat of combination of 56 grammes of carbon monoxide with 32 grammes of oxygen, *minus* the heat absorbed by the decomposition of 32 grammes of oxygen molecules into their constituent atoms. The oxygen atom does not exist alone, and whenever free oxygen takes part in a chemical change the molecules of the element are first separated into their atoms.

and of water, and the heat produced by the combustion of marsh gas, the thermal equations being—

$$\begin{aligned}&(1)\ C+O_2=CO_2+97{,}000\text{ cal.}\\&(2)\ 2H_2+O_2=2H_2O+136{,}800\text{ cal.}\\&(3)\ CH_4+2O_2=CO_2+2H_2O+212{,}000\text{ cal.}\end{aligned}$$

The difference between the thermal value of the last process and the sum of the first and second represents the heat of formation of marsh gas—

$$97{,}000+136{,}800-212{,}000=21{,}800,$$

hence we get the expression—

$$C+2H_2=CH_4+21{,}800\text{ cal.}$$