CHAPTER II

MATTER, ENERGY AND CHEMICAL COMBINATION

ALL matter, whether gaseous, liquid or solid, is composed of one or more elements, in the form of either mixtures or chemical compounds. As far as can be ascertained by the methods available to the chemist, these elements, with the exception of the radio-active elements are separate individuals and are incapable of being transformed into other elements. Each possesses certain properties peculiar to itself. If we were to take a sample of an element and were able to cut it up into the minutest particles until a degree of fineness was reached when further subdivision became impossible, we should obtain the element in the form of its molecules. Molecules are the smallest particles of an element which are capable of separate existence. Within them is stored up considerable amounts of energy, capable of doing work, if only the conditions present themselves to enable some of this molecular energy to be released. On the basis of modern views of the structure of matter, it seems that the property which is responsible for the individuality of atoms of different elements is chiefly one of the quantity of the energy associated with the inert matter.

Conditions sometimes obtain that some of the energy contained in molecules may be rendered available at the instant when molecules of reacting gases come into collision, provided that the impact is sufficiently severe. As soon as chemical combination becomes possible, the stores of energy within the opposing molecules become unlocked, and as the reaction proceeds some of the original energy is dissipated in the form of work. When chemical combination has ended, the unused energy becomes locked up again, but now in the chemical compound. It does not again become available until suitable conditions prevail and then further chemical combination occurs. It is not the matter itself of which an element is composed that furnishes it with a separate individuality, but rather the quantity of energy possessed by each of its molecules and the amount of matter contained in each molecule. Chemical examination of the compounds formed often reveals that smaller amounts of the elements than that contained in its molecules have entered into chemical combinations. In the case of many elements, these quantities are equal to one-half of the weight of the molecule. These amounts correspond to those of the atoms of the elements concerned, and thus we find that atoms, though often incapable of separate existence, are able to enter into chemical combinations. Chemical compounds are made up of atoms of different elements that are held together by virtue of the energy stored up within the molecule. Atoms are the smallest particles of an element which can combine.

Chemistry thus resolves itself into the study of chemical compounds and the study of the energy changes entailed in bringing about chemical combination. Inorganic and Organic Chemistry deal with the compounds themselves, whilst Physical Chemistry is more concerned with the energy changes. Chemical changes may often be greatly influenced by the amounts and character of energy which may be absorbed from, or emitted to, external sources by the compound, such as by direct heating or cooling, or from the radiations sent out from the sun or from a glowing substance. In recent years, much attention has been devoted to the effects of light rays on chemical re-actions, and this constitutes a branch of physical chemistry known as Photo-chemistry. Bio-chemistry, the study of life processes, embraces all branches of chemistry, in that mineral chemistry (inorganic) is involved in the question of skeleton formation, organic chemistry in regard to the compounds formed with carbon, and lastly, physical chemistry in connection with the all-important energy-factors and conditions under which chemical reactions take place.

Instead of comparing the weights of molecules of elements, chemists have accustomed themselves to compare the weights of the atoms of elements with that of the atom of oxygen. Formerly, the atom of hydrogen, being the lightest element known, was arbitrarily taken as unity, but now the oxygen atom is taken as 16, which causes the relative weight of the hydrogen atom to be 1.008 and brings the atomic weights of many other elements much nearer to whole numbers. The following table gives the comparative atomic weights of some elements found in the animal body.

Name.	*Chemical Symbol.*	*Atomic Weight.*
Hydrogen	H	1·008
Oxygen	O	16·00
Carbon	C	12·00
Nitrogen	N	14·01
Calcium	Ca	40·07
Phosphorus	P	31·04
Sodium	Na	23·00
Potassium	K	39·10
Iron	Fe	55·84
Sulphur	S	32·06
Chlorine	Cl	35·46
Iodine	I	126·92
Magnesium	Mg	24·32

It has been found by a variety of methods that the actual number of molecules contained in a volume of any gas equal in weight to the molecular weight of the gas, expressed in grams, is

606,000,000,000,000,000,000,000

This number is usually termed the Avogadro Number, in honour of Avogadro, who first enunciated the fundamental law, that equal volumes of different gases under the same conditions of temperature and pressure contain the same number of molecules. Oxygen, hydrogen and nitrogen are each diatomic gases ; in other words their molecules contain two atoms, and are therefore represented by the respective formulæ O_2, H_2 and N_2. Easy calculation reveals the astounding fact that a molecule of hydrogen weighs

0.000,000,000,000,000,000,000,003,3 gram

and also that the number of molecules present in 1 cubic inch of air is

3,000,000,000,000,000,000,000

These numbers are too great to be intelligible to the human mind, and they are even more so when considered in terms of their diameters. It has been calculated that if the molecules contained in 1 cubic inch of air under ordinary conditions could be arranged in a line touching each other the line would pass round the earth 14,000 times.

It will be an advantage at this point to learn something about the mode in which chemical compounds are formed. Combination takes place between these infinitesimally small bodies—atoms and molecules. Take the case of water. It is composed of hydrogen and oxygen, both of which are gaseous, except when they are subjected to very low temperatures and high pressures, in which case they may become liquids or even solids. The two gases can be made to unite by simply igniting a mixture with a flame or an electric spark. The molecule of oxygen and of hydrogen each contains two atoms. Yet it is found that a molecule of water contains in the gaseous state, i.e., as steam, two atoms of hydrogen and only one of oxygen. That is, it contains less oxygen than is capable of separate existence. The reason will be understood when we know that two molecules of steam were produced by the interaction of two molecules of hydrogen and only one molecule of oxygen. Expressed in the form of a chemical equation :

2 molecules of hydrogen + 1 molecule of oxygen
$2 \quad H_2 \quad + 1 \quad O_2$
$\longrightarrow$ 2 molecules of water (steam)
$\longrightarrow 2 \quad H_2O$

When carbon burns in an insufficient amount of air, the oxygen present combines to form the very poisonous gas, carbon monoxide. The reaction is

$$\underset{\text{2 atoms}}{2C} + \underset{\text{1 molecule}}{O_2} \longrightarrow \underset{\text{2 molecules of carbon monoxide}}{2\,CO}$$

Had there been more oxygen available, carbon dioxide, or as it is sometimes called carbonic acid gas, would have resulted, thus

$$\underset{\text{1 atom}}{C} + \underset{\text{1 molecule}}{O_2} \longrightarrow \underset{\text{1 molecule of carbon dioxide}}{CO_2}$$

This substance might have been formed by burning carbon monoxide with more oxygen, thus

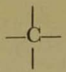
$$\underset{\text{2 molecules}}{2CO} + \underset{\text{1 molecule}}{O_2} \longrightarrow \underset{\text{2 molecules}}{2CO_2}$$

Carbon also forms by indirect methods numerous compounds with hydrogen. The simplest are: methane, CH_4; ethylene, C_2H_4; acetylene, C_2H_2; benzene, C_6H_6.

Chemists talk of the *Valency* of an element, by which they mean the number of atoms of hydrogen, or their equivalents, with which an atom of the particular element combines. Thus the valency exerted by oxygen in forming water is 2, and is therefore divalent. Let us consider the above mentioned compounds of carbon. In methane, carbon is united to four atoms of hydrogen, i.e., it is *quadri*valent; in ethylene, C_2H_4, each carbon atom is seen to be combined with two hydrogen atoms, i.e., it appears now *di*valent, whilst in both acetylene, C_2H_2, and benzene, C_6H_6, each atom of carbon is in combination with only one atom of hydrogen, and appears therefore *uni*valent. The univalency apparently indicated by carbon in acetylene and benzene will later in this chapter be shown to be not the case. It thus appears that carbon does not always exert the same valency when in chemical combination, though the maximum is seen to be four. Many other elements likewise exhibit variable valencies.

In defining valency we included the clause, "or their (hydrogen atoms) equivalents." It remains to ascertain the valency of an element when in combination with some element other than hydrogen. Perhaps the simplest example is that of carbon in carbon monoxide, CO, and carbon dioxide, CO_2. In the former compound, one carbon atom is combined with one of oxygen, whilst in the latter compound it is attached to two atoms. Oxygen, however, normally combines with two atoms of hydrogen, in other words, the equivalent of an oxygen atom is two hydrogen atoms, and therefore the valency exhibited by carbon in carbon monoxide is two, and in carbon dioxide, four.

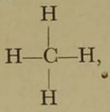
Among the large number of hydrocarbons—compounds of carbon and hydrogen—which exist, may be mentioned the succeeding four members of the methane family: ethane, C_2H_6; propane, C_3H_8; butane, C_4H_{10}; pentane, C_5H_{12}. If we were to adopt the method used in the preceding paragraphs to ascertain the valency of carbon, we should obtain 3, 8/3, 10/4, and 12/5 respectively. It would appear, therefore, that the carbon atom in the first instance was in chemical combination with three hydrogen atoms, and with fractions of the atoms in the remaining compounds. None of these conclusions are valid, for if we visualise the directions along which each valency-force acts, we find that as carbon has a maximum valency of four, the direction of each of the valency forces may be represented by a line, thus



$$\begin{array}{c} | \\ -C- \\ | \end{array}$$

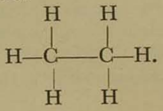
all acting in the same plane ; or (if considered in space) acting along the axes of a tetrahedron.

For the sake of simplicity, we shall consider the valencies to be acting in one plane. Then methane may be represented as



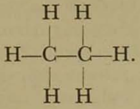
$$\begin{array}{c} H \\ | \\ H-C-H, \\ | \\ H \end{array}$$

and ethane becomes



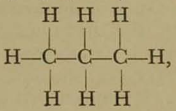
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & -\!\!-\!\!- & C & -H. \\ & | & & | & \\ & H & & H & \end{array}$$

We note a curious combination in ethane in that a valency force originating from each carbon atom is not made use of by hydrogen atoms, but that these two valencies mutually satisfy one another. Consequently, ethane is usually written



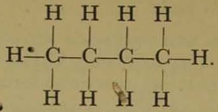
$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H. \\ & | & | & \\ & H & H & \end{array}$$

Similarly, propane, C_3H_8, may be written



$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C & -H, \\ & | & | & | & \\ & H & H & H & \end{array}$$

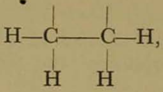
and butane, C_4H_{10}, as



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H. \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

On these grounds, we see, therefore, that the carbon atom remains quadrivalent in all these compounds.

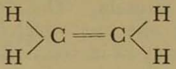
Now let us take the case of ethylene, C_2H_4. Structurally, it might be represented as



$$\begin{array}{ccccccc} & & | & & | & & \\ H & - & C & —— & C & - & H, \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

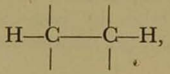
and thus we see that it possesses two valencies of which no use is being made. The compound is considered to be unsaturated, a view which gains experimental support, for when ethylene is brought into contact with an element such as bromine, bromine atoms attach themselves to these "vacant" valencies. In the presence of a catalyst, hydrogen atoms can under special circumstances be made to combine with oily bodies, which happen to be unsaturated and as a consequence of the saturating effect of the hydrogen, the oils assume the solid consistency characteristic of fats.

Seeing that ethylene is a definite chemical individual, it is considered that the pair of unsaturated valencies mutually satisfy one another. The structural formula assigned to this compound is therefore



and the linkage between the two carbon atoms is called a " double bond."

On page 8 it was suggested tentatively that the valency of carbon in acetylene, C_2H_2, was unity, but it will be seen that its structural formula, based on the combination of two potentially quadrivalent carbon atoms, will be



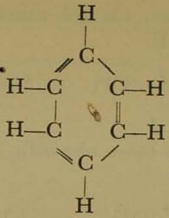
$$\mathrm{H{-}C{-}C{-}H},$$

or representing the compound as being in a temporarily stable condition, the formula may be rewritten thus :

$$\mathrm{H{-}C{\equiv}C{-}H}$$

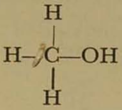
The triple bond is indicative of considerable unsaturation, and therefore of a considerable aptitude to react with other bodies. The carbon compounds, with which we have so far dealt, have been represented by straight chains of carbon atoms. Such an orientation applies to many compounds found in the living body, e.g., fats, sugar, and also to so-called mineral products as American petroleum, but it does not apply to many of the products derived from coal-tar.

If, for example, we consider the simplest compound in coal-tar, viz., benzene, C_6H_6, and still insist on giving it a structural formula based on the potential quadrivalency of carbon, we are forced to resort to a six carbon ring formula. The simplest formula so far assigned and the one which is in remarkable harmony with many of its reactions is



The concept of the quadrivalent carbon atom, in conjunction with the theory of double and triple bonds, has been the simple foundation upon which the whole fabric of Organic Chemistry has been built with such conspicuous success.

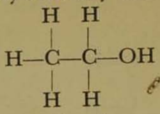
Hitherto, we have confined our attention to *hydrocarbons*, we shall now pass on to refer briefly to the *carbohydrates*. Unlike the hydrocarbons, carbohydrates contain, besides hydrogen and carbon, atoms of oxygen. The simplest class of carbohydrate is that of the "alcohols." They contain the grouping –OH attached to a carbon atom to which only hydrogen atoms are attached. If, for example, we substitute the –OH grouping for one hydrogen-atom in methane, we get



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H} \end{array} \quad \text{or} \quad CH_3OH,$$

which is methyl alcohol.

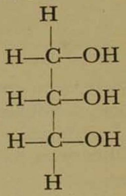
Similarly ordinary alcohol, ethyl alcohol, is



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$$

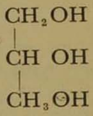
or C_2H_5OH.

Glycerine contains three alcoholic groupings, thus



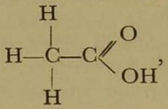
$$\begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H \end{array}$$

or



$$\begin{array}{l} CH_2OH \\ | \\ CH\ OH \\ | \\ CH_3OH \end{array}$$

An organic acid contains the grouping $\overset{O}{\overset{\|}{-C-OH}}$, which is attached, in one special case to a hydrogen atom, viz., $\underset{O}{\underset{\|}{H-C-OH}}$, formic acid, and in all other cases to a carbon atom. Thus

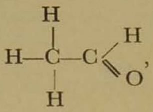


$$H-\overset{H}{\underset{H}{C}}-C\left\langle\begin{matrix}O\\OH\end{matrix}\right.$$

, or CH_3COOH

is acetic acid, the chief constituent of vinegar.

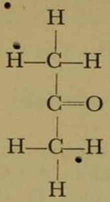
Other important groupings are those of (*a*) *aldehydes*, $-C\left\langle\begin{matrix}H\\O\end{matrix}\right.$ occupying the ends of chains, thus $H-C\left\langle\begin{matrix}H\\O\end{matrix}\right.$, formaldehyde ;



$$H-\overset{H}{\underset{H}{C}}-C\left\langle\begin{matrix}H\\O\end{matrix}\right.$$

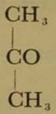
, acetaldehyde.

(*b*) *ketones*, $>C=O$, each of the valencies being attached to carbon atoms, e.g.,



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ C=O \\ | \\ H-C-H \\ | \\ H \end{array}$$

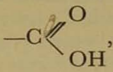
or



$$\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array}$$

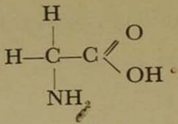
which is acetone, a volatile liquid having a peculiar odour which may sometimes be detected in the breath of persons suffering from faulty digestion of fat, a condition known as "ketosis."

Nitrogen often is to be found in compounds of carbon, hydrogen and oxygen. The family of bodies called *proteins* contains nitrogen. Protein bodies constitute the bulk of the matter contained in flesh, tissues, hair, wool, silk, and finger- and toe-nails, etc. As one may well imagine, proteins are very complicated in their structure, but investigations of their products of decomposition reveal that they must have been formed by the repeated union of organic acids having not only the characteristic acid grouping,



$-C\begin{array}{l} \nearrow O \\ \searrow OH \end{array}$

, but the amino grouping $-NH_2$, which can take the place of a hydrogen atom when attached to one of carbon. The simplest amino-acid is glycine. Its structure is



$$\mathrm{H-\underset{\displaystyle NH_2}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-C\begin{matrix}{/\!\!/}O\\ \diagdown OH\end{matrix}}$$

Now the amino group, $-NH_2$, can react with the acid grouping, $-C\begin{matrix}{/\!\!/}O\\ \diagdown OH\end{matrix}$, sometimes referred to as the carboxyl grouping, of another molecule of an amino-acid, with the elimination of water. Such a combination may be represented in the following way.

$$\underset{\text{glycine}}{\mathrm{H_2N.CH_2.CO}}\boxed{\mathrm{OH + H}}\underset{\text{glycine}}{\mathrm{HN.CH_2.COOH}}$$

$$\longrightarrow \underset{\text{glycyl-glycine}}{\mathrm{H_2N.CH_2.CO.NH.CH_2COOH}}+\underset{\text{water}}{\mathrm{H_2O}}$$

The atoms encircled by dots are liberated during the combination in the form of water. The amino grouping and the carboxyl groupings of the more complicated substance, glycyl-glycine is now at liberty to react with more molecules of amino-acids. They may be either glycine or a more complicated amino-acid, which has of course the characteristic groupings. Up to the present time, about 20 different amino-acids have been obtained from proteins. These then are the stones with which Nature builds her walls, and with the 20 different forms available—and there are certainly many more as yet undiscovered—it will be realised that very different walls will result according as and how the various materials are selected and put together. Nature is the great architect and builder. The means she adopts to select her materials is as yet unknown. The results of her labours are obvious from the nature of protein materials which she builds.

constituents of soil are hydrated silica and aluminium oxide. Silica is the oxide of the element, silicon. The pure oxide is found in various parts of the world in the crystalline state, namely as quartz. In the soil, much of it, however, exists in a kind of loose chemical combination with water, i.e., hydrated. Pure silica is now being used to manufacture a special glass—quartz-glass—which undergoes relatively little expansion on heating, so much so that red-hot silica ware may be immediately placed in cold water without the risk of fracture. Silica glass has also the remarkable property of being pervious to ultra-violet light radiations.

These compounds are examples of oxides. Although metallic aluminium can be isolated from the oxide as it occurs in the soil, when in combination with oxygen the metal loses entirely all traces of its metallic character. This is the case with all other oxides. If we consider for a moment the gases that are formed when carbon burns in oxygen, carbon monoxide, carbon dioxide, we see that these have not of the appearance of the carbon from which they were formed. Oxides, in common with all other compounds, retain some of the chemical characteristics of their constituent elements.

We have stated before, that chemical combination of elements involve energy changes. It would also appear reasonable to imagine that the energy involved in holding oxygen by one element in chemical combination would be very different from that required by another element. This can be very forcibly illustrated in the case of the oxides of aluminium and of iron, whose chemical formulæ are respectively Al_2O_3 and Fe_2O_3—the symbols Al and Fe being the

Fig. 1.—Tram-rail Welding by Thermit Process.
(*Courtesy, Messrs. Murex, Ltd., Rainham, Essex.*)

[*To face page* 21.

chemical shorthand of writing one atom of aluminium and iron (Latin, *ferrum*). Now of these two oxides, the constituents of aluminium oxide are very much more firmly held, so much so that if finely divided aluminium is mixed with powdered iron oxide, it is possible to set up conditions which will not only enable the aluminium to wrest the oxygen from the grasp of the iron, but will at the same time cause a fearfully high temperature, 3000–3500 degrees C., to be reached. With certain other oxides, e.g., the highest oxide of chromium, the chemical change takes place with explosive violence.

Incidentally, we may here mention that the conditions requisite to start this reaction were discovered by Dr. Hans Goldschmidt, and the reaction since 1898 has formed the basis of two valuable processes: one is the so-called " Thermit " process for welding steel pipes and bars, e.g., tramway rails; and the other is a method of preparing pure metals from their oxides. Metals of considerable use to-day, prepared by such a method, are chromium and tungsten. It happens that the energy changes which accompany this reaction are not spontaneously available, but become so, immediately a high temperature is established at some point within the reacting mixture. In the case of the reaction with iron oxide this can be effected by covering the charge with a layer of barium peroxide through which a strip of magnesium is passed into the aluminium—iron oxide mixture. Magnesium can readily be ignited by means of a match and burns very brilliantly in air to form a white powder, magnesia. Immediately the burning magnesium comes into contact with barium peroxide, it will burn with even greater brilliance, and in so doing will generate the necessary temperature at which the " thermit " reaction can start. Suddenly this temperature is conducted throughout the mixture and the aluminium is immediately converted into a white powder, the oxide, and the iron is released in the molten state. To make use of this molten iron to weld tram-lines together, the ends are clamped together and a mould of some refractory material, such as sand and quartz, placed carefully around the joint. The " thermit " mixture is ignited in a specially constructed crucible, having a hole in the bottom with a device for opening. This is placed above the proposed joint and the molten iron allowed to run into the gap between the two ends. " Thermit " is purchasable in tin-cans. Regarding the possibilities of this reaction, the words of Wilhelm Ostwald are very apt : " Dr. Hans Goldschmidt has given the industrial world a blast furnace and smithy for the waistcoat pocket."

Certain oxides are readily formed simply by exposing the metals to oxygen or air, and very often they will form much more rapidly should any moisture be present. This occurs in the rusting of iron. It is a curious fact that chromium combines with oxygen with great ease, yet nowadays chromium plating is finding application to protect iron and steel from corrosion. The explanation is to be found in a phenomenon which accompanies the formation of the chromium layer, in that the chromium assumes a " passive " condition, and consequently resists oxidation by air. Iron can also be rendered " passive " and then resists, for example, the attack of acids. Thus acids that contain much oxygen cause iron on immersion it in a solution of one of them to change its nature such that dilute solutions of acids, which normally dissolve it, are without effect. There is strong evidence to attribute this protection from attack to the production of a very thin, but highly resistant, layer of oxide over the surface of the metal. Usually this film is so thin that it cannot be detected by ordinary optical methods.

Some metals do not readily combine with oxygen, though under particular conditions it is possible to prepare their oxides. Such oxides, however, suffer decomposition with great ease. It is not surprising, therefore, to find these metals occurring in nature in the free state. These remarks apply to silver, gold, and the so-called "platinum metals," viz., platinum, iridium, osmium, palladium, rhodium, ruthenium. Of the 6½ tons of platinum metals produced annually, about 6 tons are obtained from the Urals in Russia. On the other hand, metals like sodium, potassium and calcium, combine with great vigour with oxygen, and it is not surprising that these metals only occur naturally in the form of their compounds. Their oxides are difficult to isolate and once prepared are very reactive.

Very few of the oxides of the metals dissolve to an appreciable extent in water. Those of sodium and potassium dissolve with ease and in so doing develop much heat. The act of dissolution involves the initial combination of the oxide with water, thus

$$\underset{\text{sodium oxide}}{Na_2O} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{sodium hydroxide}}{2\,Na\,OH}$$

to form sodium hydroxide, known commercially as caustic soda. The transformation (slaking) of calcium oxide, more commonly referred to as either "burnt lime," "quick lime" or "live lime," into calcium hydroxide before beginning to dissolve in water is more obvious, when it is remembered that by merely dropping a little water on the oxide much heat is developed, and this is accompanied by a hissing noise and a rapid swelling which eventually is superseded by the mass disintegrating into fine white particles. This is well-known to any one who has prepared "whitewash." The suspended white powder is calcium hydroxide which dissolves in water to a small degree giving "lime-water."

Relatively few hydroxides of the many metals are soluble in water, i.e., the amounts which do actually dissolve are so very small that they can only be ascertained by certain very delicate physico-chemical methods. Such a hydroxide is that of iron, ferric hydroxide, which in spite of its excessive insolubility manages to be extracted from the soil by plants. This is a wonderful fact. Vegetation obtains its nutrition from the soil-water into which the soluble substances contained in the soil texture pass. Very rarely is any iron compound found in these soil solutions except when the soil has been allowed to become very acid or "sour."

One characteristic property of the soluble hydroxides, viz., caustic soda, caustic potash slaked lime, is the slippery feeling which their solutions impart to the fingers. They also have a decomposing action on fats in forming soaps. The hydroxides have the power of combining with "acids" to form "salts," and are therefore referred to as "bases." Those bases which dissolve in water are given the name "alkalis."

Another compound, ammonia, and certain organic compounds—amines—derived from it, also possess the basic property, in that they combine with acids to form salts.

Oxides of those elements, which are not metallic, are often soluble in water and in so doing give rise to an acid solution—one which is acid or sour to the taste. This is true of the oxides formed when either carbon, sulphur or phosphorus is burnt in a plentiful supply of oxygen, or air—a mixture of chiefly oxygen and nitrogen. The oxides are carbonic acid gas, CO_2, sulphur dioxide, SO_2, and phosphorus pentoxide, P_4O_{10}. On dissolution, they give respectively, carbonic acid, H_2CO_3 ; sulphurous acid, H_2SO_3 ; and phosphoric acid, H_3PO_4. As with basic oxides in forming alkalis, so with these acid forming oxides, they unite with molecules of water to form acids. The following equations illustrate this union with water more clearly :

$$\begin{aligned} CO_2+H_2O &\longrightarrow H_2CO_3, \\ SO_2+H_2O &\longrightarrow H_2SO_3, \\ P_4O_{10}+6H_2O &\longrightarrow 4H_3PO_4 \end{aligned}$$

The rôle played by these water molecules is all important in giving rise to the alkaline or acidic nature of an oxide, in that it furnishes an explanation of the ability of certain oxides to form acids at all. It was once believed that oxygen was an essential constituent of the molecules of acids, in fact the name oxygen is derived from the Greek words meaning "I produce sourness." The German name for oxygen is *Sauerstoff*, i.e., sour- or acid-stuff. The conception that oxygen was responsible for the acidic nature of an oxide, was first propounded by Lavoisier in France in 1777. Though Berthollet demonstrated as early as 1787 that hydrocyanic acid (prussic acid, HCN) contained no oxygen, and Sir Humphry Davy in 1810 that hydrochloric acid (HCl) was a powerful acid-forming body, but contained no oxygen, Lavoisier's erroneous view prevailed for many years and has left its stamp on the system of naming acids still in vogue.

Arsenic, which can exist in a metallic state as well as in an amorphous form similar to that usually assumed by non-metals, forms two acidic oxides, namely arsenious oxide, As_2O_3, and arsenic oxide, As_2O_5. Of these, the former is the more common. Ordinary arsenical weed-killers are prepared by dissolving it in solutions of caustic soda. When in combination with lead oxide arsenic oxide forms lead arsenate—often employed as a spray to destroy fungoid growths and moths found on trees. Combined with lime both these oxides, i.e., as calcium arsenite and calcium arsenate, make a valuable insecticide, being used to destroy leaf-worm and the boll-weevil on growing cotton plants. Solutions of arsenious oxide appear to have been used for criminal purposes from the earliest times. Taken in very small quantities by human beings and animals, white arsenic, another name for the lower oxide, apparently has some stimulating effect on growth. For this reason it is often introduced into so-called tonics.

It is stated that grooms and horse-dealers sometimes include a very small amount of arsenious oxide in the daily ration of the horse, in order to assist better growth of its body and to improve its coat. Once started, such a practice must be continued, or else the doses must be very gradually reduced, otherwise the horse's condition rapidly becomes impaired. Certain peasants in lower Austria, where white arsenic is widely destributed in the earth, are reported to eat it, first by taking very small quantities and then gradually increasing the doses. Their reason appears to be that it facilitates breathing and thus enables them to climb mountains with less fatigue. Moreover, it is used in medicine in exceedingly small quantities in the case of certain chest diseases, e.g. asthma. In larger quantities it constitutes a deadly poison, leading to death in from 5 to 20 hours, during which period, faintness, nausea, vomiting and diarrhœa occur. A use to which solutions of arsenious oxide in sodium hydroxide is put is the preservation of corpses in which they are sometimes immersed for long periods in medical schools before dissection. It is a surprising thing that criminals should so often resort to such a poison, that not only may arouse suspicions before death has ensued, but one that tends to preserve the organs into which they have passed and can then be easily detected by chemical methods.

In the foregoing pages, we have described two classes of compounds which when dissolved in water acquire the property of being either an acid or a base. If one takes a solution of an alkali, sodium hydroxide say, and very carefully adds it drop by drop to a solution of acid, e.g., sulphuric acid, there will arrive a stage when the resulting solution possesses none of the characteristics of an acid, such as its corrosive action and ability to attack metals. At this point, the solution, having neither acidic nor alkaline properties, is neutralised—a state of affairs which is brought about by the formation of a salt, in the case in question, sodium sulphate. Represented chemically,

$$\underset{\substack{\text{sodium}\\ \text{hydroxide}\\ \text{2 molecules}}}{2NaOH} + \underset{\substack{\text{sulphuric}\\ \text{acid}\\ \text{1 molecule}}}{H_2SO_4} \longrightarrow \underset{\substack{\text{sodium}\\ \text{sulphate}\\ \text{1 molecule}}}{Na_2SO_4} + \underset{\substack{\text{water}\\ \text{2 molecules}}}{2H_2O}$$

Another example is the action of sodium hydroxide on hydrochloric acid (an acid present in the gastric juice) :

$$\underset{\substack{\text{sodium}\\ \text{hydroxide}}}{NaOH} + \underset{\substack{\text{hydrochloric}\\ \text{acid}}}{HCl} \longrightarrow \underset{\substack{\text{sodium}\\ \text{chloride}}}{NaCl} + \underset{\text{water}}{H_2O}$$

The action of carbonic acid gas on bases is one of great importance in connection with the chemistry of soil, water and blood. As stated earlier in this chapter, carbon dioxide on dissolution in water acquires the nature of an acid, which is represented by the formula H_2CO_3.

As we saw in the case of sulphuric acid, each of the two hydrogen atoms contained in the molecule become replaced with atoms of sodium in forming the normal salt. The reaction of sodium hydroxide with sulphuric acid may have taken place in two stages, in the first of which one hydrogen atom suffers replacement, thus

$$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$$

to form sodium bisulphate, $NaHSO_4$, and in the second, the remaining hydrogen atom in the sodium bisulphate is substituted by another sodium atom, thus

$$NaHSO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O$$

In some respects, therefore, the sodium bisulphate behaves as an acid in its ability to react with still more alkali. In like manner, sodium hydroxide reacts with carbon dioxide in solution to produce sodium bicarbonate, $NaHCO_3$, which is subsequently converted, by reacting with more alkali, into sodium carbonate, Na_2CO_3, in accordance with the equations:

$$NaOH + H_2CO_3 \longrightarrow NaHCO_3 + H_2O$$
$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$

The reaction of lime water with carbonic acid is of especial interest, in that calcium carbonate is insoluble and is consequently precipitated, whereas calcium bicarbonate is soluble. If we take a solution of carbon dioxide in water and add to it very cautiously calcium hydroxide solution, we shall observe that a certain amount of the lime water can be added before the insoluble calcium carbonate is seen to separate from solution as a white milkiness. The reaction taking place during the initial period when the solution remains crystal clear is the formation of the soluble calcium bicarbonate, $Ca(HCO_3)_2$, thus $2H_2CO_3 + Ca(OH)_2 \longrightarrow Ca(HCO_3)_2 + H_2O$.

Thereafter, the calcium hydroxide reacts with the calcium bicarbonate in accordance with the equation:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$

to form calcium carbonate, which in consequence of its insolubility separated from the solution as a white precipitate. This insoluble carbonate can be rendered soluble if only sufficient carbon dioxide can be passed into solution to form the bicarbonate once again, as will be understood by the following equation:

$$\underset{\text{insoluble}}{CaCO_3} + H_2CO_3 \longrightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}.$$

This accounts for the solvent action which water containing dissolved carbon dioxide has on limestone, whether it be in the form of chalk or marble. Much of the "hardness" of natural waters is due to the presence of the bicarbonate of calcium and sometimes of the bicarbonate of magnesium. Such "hardness" can be destroyed by boiling. This causes the bicarbonate to break up to give the insoluble carbonate, that can be filtered away, and carbon dioxide, which, owing to its much reduced solubility in water at the boiling temperature, is driven out of solution. For this reason, the "hardness" is referred to as "temporary." "Permanent" hardness is caused by the presence of salts such as calcium sulphate which cannot be forced out of the water by so simple a method.

Sulphuric and carbonic acids, each having two replaceable hydrogen atoms, are dibasic acids. We shall now consider a tribasic acid, namely phosphoric, H_3PO_4, which by virtue of its three replaceable hydrogen atoms, gives rise to three types of salts, e.g., NaH_2PO_4, Na_2HPO_4 and Na_3PO_4, thus

$$(1)\ NaOH+H_3PO_4 \longrightarrow NaH_2PO_4+H_2O$$
$$(2)\ NaH_2PO_4+NaOH \longrightarrow Na_2HPO_4+H_2O$$
$$(3)\ Na_2HPO_4+NaOH \longrightarrow Na_3PO_4+H_2O$$

The stages of neutralisation of phosphoric acid with lime-water are particularly important as they play an important rôle in rendering phosphorus available to the plant from phosphatic fertilisers, and also as they cause the insoluble calcium phosphate to be deposited at various places within the animal and human body in the form of bones and teeth. In the first place, calcium hydroxide reacts with phosphoric acid in the following way:

$$2H_3PO_4+Ca(OH)_2 \longrightarrow Ca(H_2PO_4)_2+2H_2O.$$

Unlike the other two calcium phosphates, this one is soluble in water, and crystallises from concentrated solutions as $Ca(H_2PO_4)_2,H_2O$. In its crude form, it is sold as superphosphate of lime and constitutes a valuable phosphatic fertiliser. In its pure form, it is used extensively by flour-millers in the manufacture of " self-raising flour," and also as an " improver " of flours. In making " self-raising flour it is used in conjunction with sodium bicarbonate. When dry, no reaction occurs between these two substances, but immediately they become wet, as in the making of dough, they interact. The acid phosphate behaves as an acid and liberates carbonic acid gas from the bicarbonate, which being enclosed within the dough, causes it to expand or " rise." The soluble acid phosphate of calcium, $Ca(H_2PO_4)_2$, in reacting with lime-water according to the equation, $Ca(H_2PO_4)_2 + Ca(OH)_2 \longrightarrow 2CaHPO_4 \downarrow + 2H_2O$, is converted into a less acid calcium phosphate, $CaHPO_4$, which is only slightly soluble in water. This phosphate reacts with still more calcium hydroxide to form a very much more insoluble calcium phosphate, $Ca_3(PO_4)_2$. The reaction followed may be represented by the equation : $2CaHPO_4 + Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2 + 2H_2O$. This normal phosphate of calcium constitutes the chief substance contained in the bones and teeth. It is a remarkable fact that these phosphates are carried through the body fluids in the soluble condition until they reach the seats of bone and teeth formation, where increased neutralisation occurs resulting in the separation of the normal calcium phosphate.

In all these examples of neutralisation, we see that the outcome is the production of a salt and water. The majority of salts are formed in solution. A few oxides, however, only acquire marked acid natures on heating to a temperature high enough to convert them into the molten condition when they readily combine with basic oxides. Perhaps the most important example is silica, SiO_2, which in the almost pure state is found in nature as sand. Alumina and boron trioxide are other examples. When silica is heated with oxides of sodium or potassium or even their salts, such as the carbonates or the sulphates, it becomes exceedingly reactive and forms sodium or potassium silicates. Water-glass is a viscous solution of sodium silicate. This acidic reactivity of silica towards bases is made use of in the manufacture of glass. It undoubtedly played a great part when the earth was in the molten state, so much so that many of the silicates then formed underwent crystallisation as the earth cooled. In this way, precious stones such as the emerald were formed. It may be of interest here to point out that the emerald and beryl are of almost identical composition, with the exception of very small traces of chromium oxide, which serve as the colouring agent. Both are silicates of aluminium and beryllium—the latter metal being likely in the near future to gain considerable importance in the manufacture of light alloys.